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The Ultraviolet Absorption Spectrum of Acetone Vapor[1]

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The ultraviolet absorption spectrum of acetone vapor has been photographed. The well-known absorption region in the neighborhood of 3000A, common to all ketones, is found to have on its long wave end a series of discrete absorption bands. The wave-lengths of many of these bands have been measured and a vibrational analysis is given. A second absorption region beginning about 1960A and extending toward shorter wave-lengths is found to consist of several groups of bands, the bands within each group being separated by relatively small frequency differences. The analysis of this band system may be accomplished by assuming several energy levels close together in the upper state together with four fundamental frequencies in the upper state and two in the lower. Evidence for further absorption regions extending to below 1200A has been found and the approximate positions of these regions are given. These bands evidently belong to different electron transitions from the others.

THE absorption spectrum of acetone vapor in the infrared and near ultraviolet regions has been investigated.[2] The photochemical decomposition and polymerization have also been studied.[3]

The ultraviolet absorption spectrum of acetone vapor, formerly thought to consist of a broad band of continuous absorption with a maximum about 2700A, has been shown recently by Crone and Norrish[2(e)] to have a region of discrete absorption overlying the continuum on the long wave end. In this respect, therefore, acetone shows an important resemblance to acetaldehyde.[4] A consideration of the photochemical behavior of acetone vapor led to an unsuccessful search for such a discrete absorption.[5] The fluorescence of acetone vapor would require a discrete absorption for its explanation.[6]

By use of longer absorption tubes and varying pressures the results of Crone and Norrish have been confirmed. Recently Bowen and Thompson[2(f)] have stated that the entire continuum in reality consists of fine bands and that the general overlapping of the rotational fine structure is responsible for the appearance of the spectrum. Norrish[2(g)] has objected to this viewpoint. In the present work no bands shorter than

[1] The authors wish to express their appreciation for a grant-in-aid obtained from the National Research Council.

[2] (a) V. Henri and R. Wurmser, Compt. rend. **156**, 1013 (1913); (b) V. Henri, *Etudes de Photochimie*, Gauthier Villars et Cie., Paris, 1919, pp. 74, 76; (c) C. W. Porter and C. Iddings, J. Am. Chem. Soc. **48**, 40 (1926); (d) R. Titeica, Bul. bilunar soc. fiz. romania, No. 57, 31 (1933); (e) H. G. Crone and R. G. W. Norrish, Nature **132**, 241 (1933); (f) E. J. Bowen and H. W. Thompson, ibid., **133**, 571 (1934); (g) R. G. W. Norrish, ibid. **133**, 837 (1934).

[3] Cf. reference 2(c); (a) D. Berthelot and Gaudechon, Compt. rend. **155**, 207 (1912); (b) F. W. Kirkbride and R. G. W. Norrish, Trans. Faraday Soc. **27**, 407 (1931); (c) G. H. Damon and F. Daniels, J. Am. Chem. Soc. **55**, 2363 (1933); (d) R. G. W. Norrish and Margaret E. S. Appleyard, J. Chem. Soc. **1934**, 874.

[4] See P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

[5] For mention see W. A. Noyes, Jr., Rev. Mod. Phys. **5**, 280 (1933).

[6] Cf. reference 3(c), 2(e), C. F. Fisk and W. A. Noyes, Jr., J. Chem. Phys. **2**, 644 (1934).

3027A have been observed although some search was made under conditions similar to those used by Bowen and Thompson. It is possible that higher pressures and longer exposures should be used.

Scheibe and Linström,[7] in investigating the absorption spectrum of acetone vapor in the Schumann region, have reported the existence of three bands located at approximately 51,300, 52,300 and 53,400 cm^{-1}, respectively.

The present work was undertaken with the object of obtaining a satisfactory explanation of the spectroscopic and photochemical behavior of acetone vapor.

I. The Spectrum Near 3000A

(a) Experimental procedure

The acetone used in these experiments had been purified for solubility work in the laboratory of Professor Kraus. It was fractionally distilled at reduced pressure and allowed to react with carefully dried sodium iodide. The resulting complex, $NaI.2(CH_3)_2CO$, is a convenient source of acetone.

For most of the present work a tube 30 mm in diameter and 10 meters in length was employed. Plain fused quartz windows were attached to the end by means of picein wax. A 1000 watt tungsten filament lamp was used as a source of continuous radiation, a quartz water cell being interposed to prevent undue heating. Although approximately parallel radiation was used, internal reflection prevented the intensity from falling off as rapidly as would be expected. In exposures of one-half hour a good continuum extending to about 3050A was obtained.

A few exposures were made with a one meter absorption tube and a discharge through hydrogen as a source of radiation in an effort to extend the spectrum to shorter wave-lengths.

A Hilger E_3 spectrograph was used for this region of the spectrum. The iron arc burning in air was used to furnish wave-length standards. In a few instances a mercury arc, together with a Hartmann dispersion formula for interpolation, was employed.

Great difficulty was experienced in measuring the band positions. Under the microscope it was possible to see only a very few of the strongest bands, the rest being lost in the continuum due to the magnification. Somewhat better results were obtained with a small hand microscope, although more bands could always be identified with the naked eye. The best results were obtained by use of a projection lantern and measurement on the screen. In this way most of the bands were measured.

After consideration of the appearance of the bands it was decided to measure the long wave edges rather than the centers of gravity. A few of the bands seemed to have sharp edges, but many presented a real diffuse character. In view of the faintness and the diffuse appearance of the bands, the accuracy for some of the weaker bands may not exceed 2A, although for some of the stronger bands it may be better than 1A. Each recorded measurement is the average of a large number of measurements, except for a few bands at the long wave and short wave ends of the region investigated. The accuracy may be taken as ± 10–15 cm^{-1}.

The system of discrete bands fades off into complete transmission at one end and into complete absorption at the other, so that probably all bands have not been measured. The analysis to be given predicts bands at both extremes. Some indication of bands at wave-lengths longer than those recorded was obtained, but it proved impossible to measure them with any certainty. Undoubtedly some of the faint bands in the region covered have also been missed.

It is impossible to state definitely that a real continuum is present, but we are inclined strongly to the belief that such is the case. In the one meter tube photographs were taken at pressures so low as to give nearly complete transmission down to the limit of the spectrograph without definite indication of bands at wave-lengths shorter than those recorded. The spectrum seems to be very similar to that of acetaldehyde.[4]

(b) Results

The majority of the bands observed in this region of the spectrum may be shown to fit the following three equations:

[7] G. Scheibe and C. F. Linström, Zeits. f. physik. Chemie **B12**, 387 (1931); see also G. Scheibe, F. Povenz and C. F. Linström, ibid. **B20**, 292 (1933).

$$\nu = 30923.7 + 208.6\ (v_1' + \tfrac{1}{2}) - 368\ (v_1'' + \tfrac{1}{2}), \quad (1)$$

$$\nu = 31000.9 + 216.2\ (v_1' + \tfrac{1}{2}) - 368\ (v_1'' + \tfrac{1}{2}), \quad (2)$$

$$\nu = 32121.8 + 214.3\ (v_1' + \tfrac{1}{2}) - 368\ (v_1'' + \tfrac{1}{2}). \quad (3)$$

Anharmonic terms could be included, but they would be small in any case and these empirical equations accord with the facts within the limits of experimental error. Table I shows the comparison between calculated and observed wave numbers.

One band (in addition to weak bands at longer wave-lengths which could not be measured) has not been included: 30,431.

The intensities of the bands are difficult to estimate, partly because of their faintness and probably also due to the underlying continuous absorption. In general one can say that bands with $v_1'' = 0$ are stronger than those with $v_1'' = 1$ or 2, and that the intensity is greatest when v_1' is small but not zero.

The bands obeying Eq. (3) lie in a region where the continuous absorption is quite important and this probably accounts for the fact that more members of this system were not observed. It is possible that the three bands in this system for which $v_1'' = 2$ belong in reality to another system.

TABLE I. *Near ultraviolet bands of acetone.*

v_1' \ v_1''	0 obs.	0 calc.		1 obs.	1 calc.		2 obs.	2 calc.
0	30839	30844						
1	31052	31053	(370)	30682	30685			
2	31262	31261	(367)	30895	30893			
3	31471	31470	(360)	31111	31102			
4	31682	31678	(357)	31325	31310			
5	31898	31887	(369)	31529	31519			
6	32093	32096	(366)	31727	31728			
7	32304	32304	(370)	31934	31936			
8	32502	32513	(371)	32131	32145			
9	32722	32721		*32375*	32353		*31971*	31986
10				32569.	32562			32194
11				*32785*	32771	(384)	*32401*	32403
12								32820
13							*33036*	33029
0	30925	30925	(366)	30558	30557			
1	31151	31141	(371)	30780	30773			
2	31362	31357	(377)	30985	30989			
3	31568	31574	(363)	31205	31206			
4	31798	31790	(375)	31423	31422			
5	32007	32006						
6	32213	32222						
7	32434	32438						
8	32653	32655						
9	32882	32871						
0	32045	32045						
1	32261	32259	(363)	(31898)	31891			
2	32478	32474	(385)	(*32093*)	32106			
3	32688	32688	(384)	32304	32320			
4				32545	32534	(392)	*32153*	32166
5							*32375*	32380
6							*32605*	32595

Bands in parentheses have been included twice. The assignments of those printed in italics may be considered as doubtful.

It is impossible to state whether the diffuseness is really of the predissociation type or not, as the apparent lengths of the bands change during a progression. In general the diffuse character seems to increase as v_1' increases.

(c) Discussion of results

The frequency difference of approximately 370 cm^{-1} has been assigned to the ground state for two reasons: (1) A strong Raman line has been reported of frequency from 376 to 391 cm^{-1};[8] (2) It seems necessary to use this same frequency in classifying the bands in the Schumann region.

This frequency is probably due to the motion of the acetone molecule represented schematically in Fig. 1.[9] One would expect this sort of deformation motion to have a low frequency compared to those due to ordinary bond bending and stretching.

The constants 216.2, 208.6 and 214.3 seem logically to be ascribed to the upper state. The first two differ by more than experimental error (not enough bands are observed in the third matrix to make it possible to state whether the 214.3 differs from either of the others by more than the experimental error). Tentatively these frequencies may be assigned to the same type of motion in the upper state as the 370 in the lower state. This would mean, therefore, a weaker restoring force for this type of motion in the

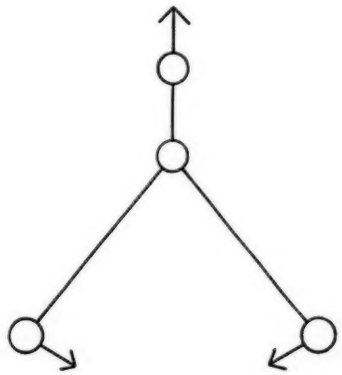

FIG. 1.

[8] Cf. K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, p. 314, Julius Springer, Berlin, 1931; K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B24**, 370 (1934).

[9] The authors wish to express their appreciation to Professor D. H. Andrews and Dr. J. W. Murray of Johns Hopkins University for communicating an interpretation of the Raman spectrum of acetone.

upper electronic state than in the lower, or in all probability a wider angle between the carbon-carbon bonds.

There remains the explanation of the difference between the 208.6 and 216.2. It has been pointed out that some of the weaker bands at longer wave-lengths may have been missed and that the correct assignment of the 0,0 band may not have been made in either matrix. The frequency difference of 77 cm^{-1} is quite low for either a deformation or a bond frequency. It seems more probable that the true difference between the frequencies of the 0,0 bands should be $77+216n$, where n is probably small (1 or 2). Thus we would have an additional frequency (necessarily in the *upper* state) of 77, 293 or 509 cm^{-1} corresponding to one of the other types of deformation vibration. To this frequency we will assign the quantum number v_2. The compounding of two deformation frequencies leads, as would be expected, to a small change in the frequency associated with v_1.

The two remaining differences between constant terms, 1198 and 1121 cm^{-1}, respectively, are open to the same doubt as the frequency corresponding to v_2. Suffice to say that both of these frequency differences are too large to be ascribed to a stretching of the carbon-carbon single bond, unless the strength of this bond is greater in the upper than in the lower state. These frequencies do fall, however, in the general region in which one finds carbon-hydrogen bending frequencies. Indeed the normal acetone molecule shows four such Raman frequencies 1220, 1354, 1423 and 1438 cm^{-1}. The exact nature of the upper electron state is unknown, but it seems improbable that the fundamental frequencies within the methyl groups would differ widely from those in the normal state. Tentatively we will accept 1198.1 as corresponding to a quantum number v_3 in the upper state. There are two reasons for not assigning it to the ground state: (1) whereas the intensities are difficult to estimate, the general appearance of the bands is such that the Boltzmann factor could scarcely be decisive in determining the relative intensities; (2) although 1198.1 differs from an accepted Raman frequency by only 22 cm^{-1}, it would be illogical to assign it to the ground state since none of the other fundamental frequencies of the ground state other than 370 seem to be necessary.

The complete description of the observed bands may be made with three quantum numbers in the upper state and one in the lower state.

Since acetone is diamagnetic the electrons in the normal state are all paired. For the upper electron state all of the spins may be paired, or the spins of two of the electrons may become uncoupled leading to the formation of a single bond between the carbon and oxygen. In the latter case one should expect to find electronic sublevels whose spacing would be difficult to predict. This would lead to the formation of many sub-bands and might give a possible explanation of the relatively small separation (frequently as small as 30 or 40 cm^{-1}) of the band heads. In this event the vibrational analysis given above would be entirely meaningless and the separation of the vibration levels would have to be regarded as unknown. It is probable that sub-bands of the type observed by Dieke and Kistiakowsky[10] for formaldehyde should also appear in acetone, but they probably would not be observed as separate bands in the present experiments.

The absorption region in question is characteristic of ketones and aldehydes and is to be ascribed in some way to the presence of the $>C=O$ group. If the electron system associated with this group is changed during absorption, the carbon-carbon valences will also be affected and the stable angle between these valences will differ from that in the normal state. An application of the Franck-Condon principle leads one to predict that the most intense bands should occur when the change in v_1 is greater than zero. This is in accord with the facts presented above.

Since the absorption region in question corresponds to about four electron volts, more than enough energy is being provided to dissociate the carbon-carbon bond and nearly enough to dissociate a carbon-hydrogen bond. If either type of bond is to be broken as a result of predissociation two explanations are possible: (1) There exists another electron state of the acetone molecule whose polydimensional surface describing the various types of vibratory motion intersects

[10] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

that of the upper state of the present band system. The bands might or might not be diffuse depending upon the way in which the two surfaces intersect. The predissociation process would be described in terms similar to those used in discussing unimolecular reactions. (2) The process may be very similar to that described in (1), but the electron term for the present band system would be less than the energy of dissociation of one of the bonds. Rearrangement of the vibrational energy alone, without the presence of an additional electron state, might then lead to dissociation. Here again the absorption bands might or might not be diffuse depending upon the nature of the energy surface. Of course predissociation by collision may be important. Final decision with regard to the mechanism of dissociation must await information from other sources.

II. The Spectrum in the Far Ultraviolet

For the bands in this region a one meter focus glass grating was used. There were 30,000 lines to the inch and the dispersion was 8.52 A/mm in the first order. For part of the work the continuum from an uncondensed discharge in hydrogen was used. The discharge took place in a 1.5 mm capillary tube and the continuum was entirely free from lines down to the beginning of the Lyman bands.

As wave-length standards the nitrogen doublet (1745.260; 1742.740) and the 1931.027 line due to C III were used. The former were superimposed by passing nitrogen through the discharge tube for a short time and the latter occurred merely due to impurities in the gas. The first strong line in the Lyman bands (1644.48A) could be used as an auxiliary standard.

Since the grating was used at nearly normal incidence the dispersion was nearly independent of wave-length and interpolation could be made directly. Table II shows values for the dispersion obtained on a characteristic plate.

For a continuum below 1650A, a condensed discharge in hydrogen was used. An 8 mfd. condenser, fully charged to 3000 volts by a d.c. generator, was discharged twice a second through a 1 mm capillary by means of a rotating contact. This gave a satisfactory continuum throughout the Schumann region with lines of silicon, carbon and boron superimposed. Neither hydrogen lines nor lines from the aluminum electrodes appeared.

Table II. *Dispersion of grating spectrograph.*

Distance	Wave-length		Dispersion
(mm)			
$a-97.140$	1931.027	$a-b$	8.5343
$b-75.373$	1745.260	$a-c$	8.5321
$c-75.072$	1742.74	$d-a$	8.5305
$d-63.549$	1644.48	$d-b$	8.5233
		$d-c$	8.5273
		Average	8.5295 ±0.0034 (0.03%)

For those plates on which the nitrogen lines and the carbon line were not present, the wave-lengths of a few prominent lines were determined with reference to previously determined bands of acetone. Thus the wave-lengths of all of the bands are determined either directly or indirectly with respect to the standards mentioned above. While the absolute wave-lengths as given in the table may be subject to some inaccuracies, the relative values should probably be good to 0.1A for the strong sharp bands and be somewhat less accurate for the others.

It was possible even with the capillary sources to cover about 3/4 of the grating (ruled surface 4.25 in.); accordingly the resolving power was quite large.

In some experiments the spectrograph containing acetone vapor was separated from the discharge by a fluorite window. This served the double purpose of removing the second order hydrogen bands (which came out quite intensely) and preventing the acetone vapor from diffusing through the slit into the discharge. Exposure times were always less than a half hour (only a few minutes with the condensed discharge) so that it was not necessary to pump acetone through the spectrograph. In other experiments no window was used. A slight amount of acetone was probably pumped through the slit in this case, but caused no trouble in the condensed discharge.

The absorbing column was about two meters in length and hence the acetone pressures required were extremely low. The appearance of the bands depended greatly on pressure, so that it was necessary to take a long series of exposures

TABLE III. *Acetone bands 2000–1800A.*

1. Number of times measured; 2. wave-length (A); 3. average deviation from mean; 4. frequency (cm^{-1}); 5. pressure (mm); 6. estimated intensity.

1	2	3	4	5	6	1	2	3	4	5	6
1	1995.50	——	50113	50	00	9	1917.12	0.13	52162	0.025	4
5	1962.67	0.10	50951	0.28	0	3	1916.27	0.06	52185	0.015	6
11	1960.78	0.08	51000	0.015	6	15	1914.99	0.11	52220	0.005	9
7	1960.05	0.08	51019	0.015	6	10	1914.21	0.09	52241	0.005	9
6	1958.82	0.09	51051	0.015	6	6	1912.69	0.17	52282	0.005	9
4	1957.98	0.14	51073	0.02	4	6	1909.66	0.09	52365	0.0075	8
14	1956.58	0.15	51110	0.015	6	4	1907.38	0.09	52428	0.0075	8
20	1954.22	0.14	51171	0.0025	10	3	1905.92	0.04	52468	0.0075	8
11	1953.30	0.12	51195	0.005	9	4	1884.36	0.11	53068	0.08	2
3	1952.15	0.07	51226	0.0075	8	3	1881.94	0.07	53137	0.08	2
4	1951.33	0.11	51247	0.005	9	7	1878.42	0.18	53236	0.035	3
7	1949.89	0.24	51285	0.005	9	11	1877.55	0.16	53261	0.035	3
3	1943.86	0.07	51444	0.015	6	12	1872.42	0.10	53407	0.015	6
5	1942.05	0.09	51492	0.015	6	3	1870.27	0.07	53468	0.035	3
3	1941.12	0.13	51517	0.015	6	5	1868.88	0.12	53508	0.015	6
2	1939.82	0.30	51551	0.015	6	2	1866.67	0.25	53571	0.035	3
3	1938.89	0.18	51576	0.015	6	1	1841.85		54293	0.13	0
6	1927.18	0.08	51889	0.025	4	9	1836.96	0.15	54438	0.122	1
3	1926.38	0.05	51911	0.035	3	5	1835.07	0.23	54494	0.13	1
8	1925.25	0.17	51941	0.035	3	2	1833.29	0.03	54547	0.218	0
5	1922.95	0.10	52003	0.035	3	5	1831.15	0.10	54611	0.122	1
6	1921.11	0.12	52053	0.02	4	5	1829.12	0.08	54671	0.114	1
3	1918.94	0.06	52112	0.02	4	5	1826.91	0.07	54737	0.130	1
						2	1819.71	0.01	54954	0.16	0

at pressures ranging from 0.0025 to 0.15 mm in pressure intervals of 0.005 mm.

Since a few of the bands seemed to have wave-lengths corresponding fairly closely to those reported for methyl iodide by Scheibe, Povenz and Linström,[7] the entire spectrum was rephotographed, using acetone which had not been subjected to the second purification by sodium iodide. The agreement between the bands observed with commercial C.P. acetone purified with sodium iodide and fractionally distilled in vacuum and the bands obtained with acetone from the laboratory of Professor Kraus was complete.

(a) Results

Beginning about 1960A and extending down to nearly 1800A a great many bands have been observed and the wave-lengths measured. The wave-lengths and wave numbers of these bands are given in Table III.

Because of the fact that the bands tend to become diffuse in appearance as the pressure is increased, the accuracy of the measurements is usually greatest at nearly the lowest pressure at which a given band can be observed. Also for this reason a slightly displaced wave-length may be observed at higher pressures which, without care, may be taken as the wave-length of a new band. In general it proved unsafe to classify bands close together as separate bands unless they were observed on the same spectrum.

The bands were always shaded toward the violet so that the wave-lengths are those of the long wave edges. Fig. 2 shows a reproduction of two spectra.

The intensities (given on a scale of ten) are estimated from the appearance of the bands and the pressures at which they are first observed.

(b) Description of bands

An examination of the plates covering an extended pressure range shows that there are four well defined regions of absorption above 1800A which tend to merge as the pressure is increased. On the long wave end of the band system there is complete transmission persisting to the saturation pressure of acetone vapor at room temperature. Below 1800A there is also a transmission region up to this same high pressure, although some continuous absorption shows up here at high pressures. Below 1664A there are undoubtedly other band systems.

Three absorption regions separated by 1000–

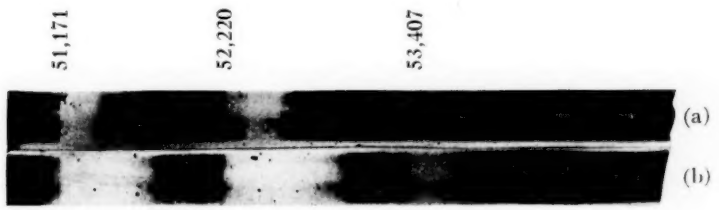

FIG. 2. Acetone absorption bands. (a) $p=0.002$ mm. (b) $p=0.045$ mm. Enlarged $2\frac{1}{2}$ times.

1200 cm^{-1} were noted by Scheibe and Linström[7] who considered them single bands due to the low resolving power employed. The fourth region appears only at relatively high pressures (above 0.1 mm). As the pressure is increased by steps new bands appear both to the red and to the violet in each of the three first regions. New bands to the red appear more slowly than do those on the violet side and the former remain closer to the low pressure bands than do the latter. The original low pressure bands become more diffuse as the pressure is increased. A pressure is then reached for each region beyond which no new bands appear, although a transmission region still exists between each pair of adjacent band groups. These intermediate transmission regions disappear at still higher pressures. This behavior of the bands with pressure indicates that a slight continuous absorption is present in the entire region rather than that new bands or new branches to the original bands are appearing so close together that the structure is obscured.

While the grating is not adequate to resolve possible rotational lines in the bands, it should be capable of showing rotational branches if such exist. Since the moments of inertia in acetone are approximately equal (one about double the other two), widely separated branches such as are observed in formaldehyde[10] would not be expected. Several bands were, however, observed which were separated by about 20 cm^{-1} from strong bands. These would appear to be branches of the strong bands. Examples are 51,019 and 51,000, 51,195 and 51,171, 52,241 and 52,220.

The question of predissociation is of interest, especially in respect to the photochemical decomposition of acetone in this region. None of the bands have the appearance of predissociation bands, excepting possibly those of frequency greater than 54,293. These are diffuse even at the lowest pressure observed. Continuous absorption, while it seems to exist, is very much weaker than that between 2500 and 3200A.

(c) Analysis of the bands

A close examination of the regions separately shows no obvious grouping of the bands in progressions or sequences. However it is apparent that a band group in one region is very similar to a group in the next region and often this similarity is repeated in a third region. This shows that the vibration frequency differences must be large and of the order of 1000 to 1200 cm^{-1}. After a search for constant differences it was found that these numbers were 1052 ± 4 and 1194 ± 7 cm^{-1}. In addition a few bands showed differences of 717 ± 2, 321 ± 1, 381 (used once) and 493 ± 2. 1052, 1194 and 717 seemed most surely to be upper state differences while 381 and 493 belong probably to the lower state since they are well-known Raman frequencies in acetone.[8]

The very large numer of bands throughout the four regions separated by 50–60 cm^{-1} led finally to the discovery that all the bands could be classified in three systems whose lowest levels in the upper state differ by 55 and 59 cm^{-1} respectively. The connection between these three levels is somewhat doubtful, but a triplet electronic upper state is not out of the question.

The arrangement of the bands is presented in Table IV. The transitions from the ground level to the three lowest levels in the upper state are 51,171, 51,226 and 51,285 cm^{-1}. The higher levels in the upper state are obtained usually as differences from 51,171 and 51,226 with the above mentioned frequencies. 51,285 shows only one difference, 1183, but we could not classify these two bands in any other way. The assignment of 52,003 is very doubtful on the basis of intensity.

TABLE IV. *Classification of acetone bands (2000–1800A).*

		51171 } 51195 }				
1194 52365	1049 52220 } 52241 }	718 51889 } 51911 }	321 51492 } 51517 }	(492)	51000 } 51019 }	
1143 53508	1016 53236 } 53261 }				1053 52053	
1103 54611					1015 53068	
	52220 } *52241* }				*51000*	
	1187 53407				1185 52185	
	1140 54547		*51492* } *51517* }	(382)	51110	
	53236 } *53261* }				1052 52162	
	1202 54438					
		51226 } 51247 }				
1202 52428	1056 52282	715 51941 (497)	51444 (493)	50951	325 (51551) } 51576 } (500)	51051 } 51073 }
1143 53571			1052 52003		1061 52112	
1100 54671					1025 53137	
52428		51285				
1040 53468		1183 52468				
1026 54494						

The bands at 54,737 and 54,954 could not be classified except by the use of very high and different frequencies. In the case of bands with two branches the differences were taken for the low frequency heads.

The band 50,113 seems to be a case by itself and very probably arises from a high level in the ground state. The difference 51,171 − 50,113 is 1058.

(d) Discussion

Several points in regard to the classification of the bands may be emphasized. The frequency differences in a progression decrease rather rapidly with increasing quantum number. Since the number in a progression is never over three, second differences must be compared in corresponding progressions as 51,051–52,112–53,137 and 51,000–52,053–53,065. The constancy of these differences supports the classification given.

The numbers in the upper state are most certainly modifications of Raman frequencies 391, 787, 1066 and 1220.[8] The first is used and discussed in the classification of the near ultraviolet bands; 787 is associated with symmetrical stretching of the molecule;[9] 1066 is an unsymmetrical stretching of the molecule, one methyl and the oxygen atom moving toward the center of gravity and the other methyl and the central carbon atom moving away; 1220 is due to change of the angle between the carbon-hydrogen bonds. The frequency 381 in the lower state is certainly the Raman frequency 391 and 492 is the Raman frequency 486. The latter does not appear in the upper state.

Decreases take place in the fundamental frequencies when they appear in the upper state, this being least in the case of 1066 and 1220 and greatest in the case of 391 and 787. The change in regard to the change of 391 to 322 is analogous to that present in the near ultraviolet bands, although for some reason the restoring force is nearer the normal value and the angle between the carbon-carbon bonds is not so wide. It would appear that this type of motion may be compounded with higher frequency motions since bands separated by 1052 and 1194 are also separated ultimately from the origin by the difference 321.

A decision as to which of these types of motion would lead most easily to disruption of the molecule is impossible, but certain generalizations may be stated. The 787 motion could scarcely lead to the breaking of a single bond. In any case progressions involving this frequency are all short. The 1220 motion alone might, if carried to convergence, lead to the rupture of the carbon-hydrogen bond, but series involving this frequency converge relatively slowly and do not extend beyond a quantum number of three (the approximate convergence limit would be 65,000 cm^{-1}). The progressions based on 1052 converge at about the same rate, but extend only a very short distance. This motion might eventually lead to the rupture of a carbon-carbon bond. Unless some repulsive perturbing state exists so that dissociation could result by predissociation, rupture of any of the bonds in the acetone molecule by the absorption of radiation in this region would seem improbable. Whether the

apparent slight continuous absorption mentioned above gives evidence for such a perturbing state is uncertain.

In conclusion, it seems that rupture of a carbon-carbon bond by absorption in this region would be most probable, and the rupture of a carbon-hydrogen bond the next most probable case. Experiments by one of us (W.M.M.) indicate that relatively more hydrogen is produced in this region of the spectrum than at longer wave-lengths. Hydrogen must come from the splitting of a carbon-hydrogen bond in the primary process. However it is impossible to decide whether the hydrogen comes from predissociation or from the continuous absorption observed in this region. Perhaps a decision could be made by the use of strictly monochromatic light in the band region, although this seems doubtful. Results obtained at relatively low pressure indicate that collision phenomena are not solely responsible for the production of hydrogen.

III. The Absorption Below 1800A

The data in this region are still incomplete and will be made the subject of a future article. With the present setting of the grating the region from 2200 to 1250 is covered in the first order. Without a fluorite window the hydrogen bands from 1100 to about 900A appear at one end of the plate in the second order, with the uncondensed discharge, while in the condensed discharge strong lines in these bands appear in absorption. When acetone is present all of the second order is removed by continuous absorption of acetone from 1100 to 900A, the probable actual limit being at even shorter wave-lengths.

The bands given in Table V have been found between 1250 and 1700A. An analysis will not be attempted until this region is covered more thoroughly.

Table V. *Acetone bands bewteen 1700 and 1250A*

1. Number of times measured; 2. wave-length (A); 3. average deviation from mean; 4. frequency (cm^{-1}); 5. pressure (mm).

1	2	3	4	5
2	1710.4	0.12	58466	0.02
11	1664.9	0.40	60065	0.03
1	1636.6		61104	0.053
2	1630.5	0.11	61332	0.053
1	1620.5		61710	0.053
2	1608.4	0.32	62173	0.053
1	1600.6		62477	0.053
1	1380.1		72458	0.0025
1	1378.9		72519	0.0025

The bands in Table V show some differences similar to those found in Section II. The following may be mentioned in particular:

72519 − 72458	61	62477 − 61332	1145
62477 − 62173	304	62173 − 61104	1069
62477 − 61710	767	61104 − 60065	1039

In conclusion the authors express their appreciation to Dr. E. J. Hart who carried out some of the measurements reported in this paper.

A Comparison of the Photosensitized Reaction of Hydrogen and Oxygen, and Deuterium and Oxygen

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(Received July 17, 1934)

The rates at which hydrogen-oxygen and deuterium-oxygen mixtures react when illuminated in the presence of mercury vapor, have been measured. There is found to be very little difference between the rates under these conditions and the temperature coefficients of the two reactions are, to within the accuracy of this work, equal. Various mechanisms are discussed in the light of this experimental observation.

INTRODUCTION

IN a recent communication Bates[1] has reviewed and discussed critically the several theories which have been advanced to account for the kinetics of the mercury photosensitized reaction between hydrogen and oxygen. Since the reaction is photosensitized the discussion is concerned with the fate of the hydrogen atoms which are produced as a first step in the reaction.

The atomic hydrogen is formed by the "quenching" of excited mercury atoms in the $^3P_1$ state by molecular hydrogen; this however, will not be the only deactivating process and oxygen will also quench the excited mercury atoms bringing about a deactivation of the mercury and an excitation of the oxygen molecules.

The fate of the hydrogen atoms so produced is now generally conceded to be a reaction between hydrogen atoms and oxygen molecules, $H+O_2 \rightarrow HO_2$. The HO_2 complex so formed may react in the following ways:

1. $HO_2+H_2 \rightarrow H_2O+OH$,
2. $HO_2+H_2 \rightarrow H_2O_2+H \quad k_2$,
3. $HO_2+HO_2 \rightarrow H_2O_2+O_2 \quad k_3$.

The reaction scheme proposed by Bates involves the use of reactions 2 and 3 and leads to an expression for the rate of hydrogen peroxide formation of the form

$$\frac{d[H_2O_2]}{dt}=\frac{k_2}{k_3^{\frac{1}{2}}}[H_2]\left\{\frac{k_H[H_2]I}{k_H[H_2]+k_0[O_2]}\right\}^{\frac{1}{2}}+\frac{k_H[H_2]I}{k_H[H_2]+k_0[O_2]}, \quad (1)$$

where the expression $k_H[H_2]I/(k_H[H_2]+k_0[O_2])$ is a measure of the ratio of the quenching of excited mercury atoms by hydrogen to the total quenching by the mixed hydrogen and oxygen.

Bates has demonstrated that the above equation is adequate in explaining the known facts concerning the rate of hydrogen peroxide production from hydrogen and oxygen. It has sometimes been assumed that in cases where a large percentage of the products was not found to be hydrogen peroxide that under such experimental conditions hydrogen peroxide was first formed and that it subsequently decomposed into water and oxygen.

The above expression does not, however, explain the observed experimental facts when hydrogen and oxygen photosensitized by mercury vapor and illuminated by mercury resonance light are allowed to react in a static system at relatively low temperatures. Barak and Taylor[2] studied the reaction under such conditions and made the following observations: (a) The rate curves obtained by plotting decrease in pressure against time of illumination were slightly autocatalytic in form. The increase in reaction rate as the reaction proceeded being more marked as the proportion of hydrogen in the mixture was increased. (b) Analysis of the reaction mixture during the course of the reaction always showed a 2 : 1 ratio of disappearance of hydrogen to oxygen and no peroxide could be detected in the reaction system. (c) The average rate of reaction was greatest for the 2 : 1 ratio of hydrogen to oxygen and decreased as the proportion of either constituent was increased.

Bates points out that his expression leaves the

[1] Bates, J. Chem. Phys. **1** (7), 457 (1933).

[2] Barak and Taylor, Trans. Faraday Soc. **28**, 569 (1932).

results of Barak and Taylor "entirely unexplained" and suggests that in this case of a static system the mechanism is complicated by diffusion processes. The present research was carried out over a temperature range of 20°C to 50°C and using both hydrogen and deuterium-oxygen mixture in the hope that a comparison of the rates of reaction in both cases might give some clue to the mechanism of reaction under these conditions.

Experimental

1. Apparatus

The experiments were carried out in a circulatory system shown in Fig. 1. The reaction vessel

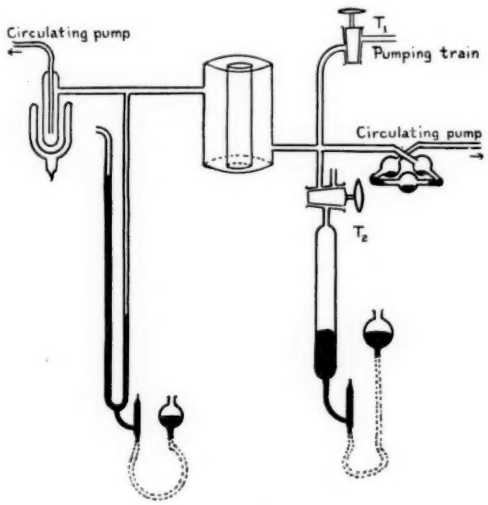

Fig. 1.

was an annular quartz cylinder connected on one side to a manometer and trap and on the other side to the pumping train and gas train. The reaction vessel was so constructed that the mercury arc could be inserted through the center of the cylinder and hence the maximum amount of light was incident upon the reaction vessel. The gases which were circulated through the system passed through mercury bubblers before entering into the reaction vessel. These mercury bubblers were maintained at a constant temperature slightly higher than that of the reaction vessel in order to saturate the gases with mercury vapor. The gases leaving the quartz reaction vessel passed through a trap which was cooled in liquid air and here any condensible products of reaction were removed. Tap T_1 led to the pumping train which consisted of a mercury vapor pump backed by an oil pump and by means of tap T_2 the gases could be admitted to the apparatus. The reaction vessel and arc were bathed in a thermostat which was maintained at a constant temperature to 0.1°C during the course of an experiment.

2. The arc

The arc employed was a Hanovia resonance lamp run off 5000 volts and 30 milliamp. This lamp was exceedingly rich in the resonance line 2537A as was indicated by a spectrum analysis of the light which showed it to be almost exclusively the resonance line. During the course of the work it was found that the intensity of the light remained exceedingly constant and reproducible results could be obtained under identical experimental conditions of pressure and temperature even after many running hours of the arc.

3. Propagation of the gases

In all these experiments the ratio of hydrogen to oxygen was 2 : 1 and the electrolytic gas was prepared by the electrolysis of caustic potash solution. This solution was electrolyzed in a glass cell with nickel electrodes and the cell cooled in ice. Before the preparation of any gas the cell was evacuated and then the first gas evolved was allowed to escape before a sample was collected. The gases so prepared were passed over several tubes containing phosphorus pentoxide and then admitted to a storage bulb.

The deuterium oxygen mixture was prepared by electrolysis of heavy water of the greatest density available; a little sodium metal was added to the pure heavy water to confer conducting properties upon the solution.

4. Experimental procedure

The gases were introduced into the apparatus and with the bath, mercury bubblers and the liquid air cooled trap at steady temperatures the gases were circulated by means of a circulation pump until constant pressure readings were obtained on the manometer. It was necessary, in order to avoid fortuitous fluctuations in pressure,

to maintain a constant level of liquid air round the condensation trap. The circulating pumping system caused merely a very small oscillation of the mercury columns in the manometer limbs, the amplitude of the rise and fall of the mercury meniscus being of the order of 0.2 to 0.3 mm. It was possible to estimate the mean position of the mercury level to an accuracy of about 0.2 mm. When under the conditions of the experiment constant readings of the pressure of electrolytic gas in the system had been obtained over a period of half an hour, the mercury resonance arc was switched on and pressure readings taken every minute.

Experimental Results

The early experiments were carried out at temperatures of about 15–20°C and some of these results are shown graphically in Fig. 2. These curves show an induction period and the general shape of the curve is one of increasing rate as the reaction proceeds. These observations are in agreement with the work of Barak and Taylor who obtained similar curves under comparable conditions in a static system. It was suggested at the time that this form of curve was due to the static system which these workers used and that

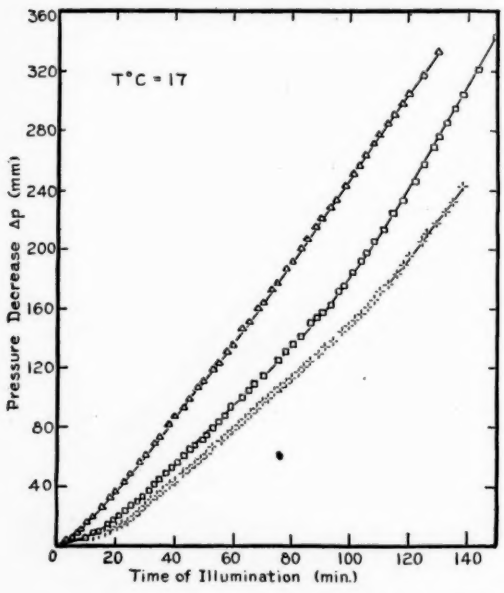

Fig. 2. The increased induction period on successive experiments without removing mercuric oxide. Pressure of electrolytic gas, 520 mm.

the complex diffusion processes which were entering in would disappear when the reaction was carried out in a circulating system. This explanation cannot account, therefore, for these results.

During the course of reactions carried out at temperatures between 15–20°C it was observed that large amounts of mercuric oxide were formed and deposited on the walls of the reaction vessel where the gases entered the illuminated zone and also on the surface of liquid mercury present in the reaction vessel.

If then further experiments were carried out without first removing the mercuric oxide the subsequent reactions showed increasingly longer periods of induction and the overall reaction rate was much slower. The coating of mercuric oxide could be removed by illuminating the vessel with mercury resonance light while circulating hydrogen through the system when the atomic hydrogen produced removed the oxide of mercury. If this cleaning procedure were adopted between experiments it was possible to obtain fairly reproducible results.

The comparisons between the rates of hydrogen-oxygen and deuterium oxygen mixtures were carried out over a higher temperature range 30–50°C and in this range practically no induction period was observed; the vessel was cleaned of mercuric oxide between experiments but the amount of mercuric oxide found at these higher temperatures was considerably smaller than between 15–20°C.

Fig. 3 shows typical reaction curves for hydrogen-oxygen and deuterium-oxygen mixtures in which the pressure decrease Δp in millimeters is plotted against the time of illumination in minutes. It will be observed that the rates of reaction whether for hydrogen or deuterium-oxygen mixtures are under these conditions practically constant from the start of the reaction and show a slight falling off from linearity only towards the end of the reaction.

One also observes both from Fig. 3 and Table I that there exists very little difference between the rates of reaction for the hydrogen or deuterium-oxygen mixture. In order to establish the reality of these small differences it was necessary to obtain a degree of reproducibility for the hydrogen-oxygen reaction which was very much

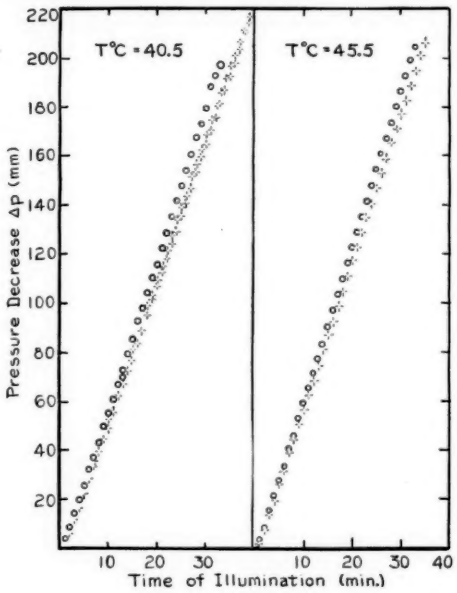

FIG. 3. Typical examples of the difference in rate between hydrogen-oxygen and deuterium-oxygen mixtures. Circle dot, hydrogen oxygen 2 : 1; plus, deuterium oxygen 2 : 1.

TABLE I.

Gas mixture	Temp. °K	Slope $\frac{dp}{dt}$ mm min.$^{-1}$	Gas mixture	Temp. °K	Slope $\frac{dp}{dt}$ mm min.$^{-1}$
Hydrogen + oxygen 2 : 1	303.5	5.25	Deuterium + oxygen 2 : 1	303.5	5.03
	308.5	5.50		308.5	5.19
		5.43			5.27
		5.52			
		5.57			
		5.50			
	313.5	5.94		313.5	5.64
		5.98			5.67
	318.5	6.30		318.5	6.05
	323.0	6.76		323.0	6.37

greater than these differences between the hydrogen and the deuterium reaction. In Table I the results for the temperature 308.5°K indicate the reproducibility which could be obtained. When comparisons between hydrogen and deuterium were being made the experiments were carried out alternately each experiment being repeated at least three times under the same conditions. Moreover the constancy of the light intensity of the mercury resonance lamp was frequently tested by repeating the hydrogen and oxygen reaction under definite conditions and at the first working temperature 30°C.

From the change in slope of the rate curves with temperature it is possible to obtain the temperature coefficient for the reaction over the restricted temperature range studied. The data for this determination are shown in Table II and

TABLE II.

$\log_{10}$ rate hydrogen	0.7202	0.7419 0.7460	0.7740 0.7773	0.7998	0.8301	Energy of activation for both systems $E = 2500$ cal.
$\log_{10}$ rate deuterium	0.7016	0.7150 0.7220	0.7513 0.7540	0.7818	0.8041	
$1/T \times 10^{-2}$	0.3305	0.3252	0.3200	0.3150	0.3096	

to within the experimental accuracy of this work the temperature coefficients of the two reactions with hydrogen or with deuterium are the same and lead to an energy of activation of the process of 2500 cal., a value which is comparable to the value of 3000–5000 obtained by Taylor and Salley[3] for the low temperature range of their investigation. Under these experimental conditions the product of reaction was water as in the work of Barak and Taylor.

DISCUSSION OF RESULTS

Although the kinetic expression developed by Bates is not applicable to these experiments it is of interest to speculate upon the possible differences between hydrogen and deuterium which one might expect under experimental conditions where Bates' expression is applicable. The differences we should expect to observe between the rates would depend upon the following factors. (a) A difference in the quenching of excited mercury in the $^3P_1$ state by hydrogen and deuterium, k_{H_2}. The author has shown that hydrogen and deuterium have apparently the same quenching efficiency for excited mercury atoms so that no difference in rates of reaction could arise from this factor.[4] (b) The value of k_2 which is associated with the reaction $HO_2 + H_2 \rightarrow H_2O_2 + H$. One would expect this constant to be sensitive to the change from hydrogen to

[3] Taylor and Salley, J. Am. Chem. Soc. **55**, 96 (1933).
[4] Evans, J. Chem. Phys. **2**, 445 (1934).

deuterium since this reaction involves the breaking of the H−H or D−D bond. Neglecting the possible differences in zero-point energy in the activated state this would introduce a difference in activation energy which would be the full difference in zero-point energy between hydrogen and deuterium, 1.8 kg cal. and also a very much smaller change in activation energy due to the difference in energy level of the HO_2 and DO_2 molecules. Hence we should expect a much smaller value of the constant k_2 when deuterium is employed instead of hydrogen. (c) The value of k_3 for the reaction $HO_2+HO_2 \rightarrow H_2O_2+O_2$. It is difficult in this case to assess the difference one would expect due to the difference in zero-point energy of the $H-O_2$ and $D-O_2$ bond. The HO_2 or DO_2 molecule has been formed by a bimolecular association reaction and contains in all probability the energy of reaction distributed between the various degrees of freedom in the molecule. If the newly formed HO_2 were to react very soon after its formation it is probable, because of the large amount of energy which the molecule possesses, that the H−O bond would be in a high vibrational level, and since the difference due to the isotope mass effect decreases with increasing vibrational quantum number, we should not expect in comparing the hydrogen and deuterium reactions the full difference due to zero-point energy between the H−O and the D−O bonds to be made manifest. If however the HO_2 or DO_2 suffers a stabilizing collision before entering into reaction, we should then expect the full difference in zero-point energy to be made manifest.

Any mechanism advanced for the reaction must be able to account for (1) the constant rate against time of illumination for experiments carried out at moderate temperatures; (2) the induction period which is made manifest at ordinary temperatures; (3) the close similarity between the rates of reaction by using hydrogen or deuterium.

The large amounts of mercuric oxide which were formed on the surface of the mercury and the walls of the reaction vessel during the course of the experiments at ordinary room temperatures inclines one to the belief that under these conditions the mechanism of reaction is one which involves the alternate oxidation and reduction of mercury and mercuric oxide,[5] and that the induction period is in some way connected with the formation of a critical concentration of mercuric oxide which at the ordinary temperatures takes an appreciable time to build up.

We will now discuss the reactions which may take part in such a scheme of alternate oxidation and reduction. (1) The production of excited oxygen molecules by the quenching of excited mercury atoms by normal oxygen molecules. $Hg'+O_2 \rightarrow Hg+O_2'$. The evidence is strongly in favor of this reaction occurring by virtue of the excitation of the oxygen molecule from a $^3\Sigma$ level to a $^1\Sigma$ level, the conservation of spin momentum being maintained. Zemansky[6] has suggested that the quenching process may be due to the production of mercuric oxide. The excited oxygen molecules will now undergo several reactions probably producing ozone to some extent. If, however, an excited oxygen molecule were to collide with mercury atoms there would be ample energy available to bring about the formation of mercuric oxide. $Hg+O_2' \rightarrow HgO+O$. This reaction may not be brought about directly by the excited oxygen atoms but may be formed from the ozone which is produced when oxygen is illuminated in the presence of mercury vapor by 2537 resonance light.[7] If the rate of oxide formation is the rate governing process then we naturally would not expect to observe any difference between the rates of reaction when hydrogen or deuterium were present. Such a mechanism would not be in accordance with the observation that the maximum rate of reaction is given by the $2H_2 : 1O_2$ mixture but would imply that the rate should increase with increasing oxygen concentration. The other process which may occur is the reduction of the mercuric oxide by the atomic hydrogen, a process which may occur in two steps, the first being the reduction of the mercuric oxide to the hydroxide $HgO+H \rightarrow HgOH$ and secondly the further reduction of the hydroxide to mercury and water

[5] Bates came to a similar conclusion in J. Chem. Phys. **1**, 457 (1933).

[6] Zemansky, Phys. Rev. **36**, 919 (1930).

[7] Dickinson and Sherrill, Proc. Nat. Acad. Sci. **12**, 175 (1926). These workers observed that the production of ozone was accompanied by the formation of mercuric oxide.

$HgOH+H \rightarrow Hg+H_2O$. If such reactions do take part in the mechanism as rate determining reactions they will be of great interest.

It has been pointed out by Polanyi[8] that in the case of reactions occurring with an activation and involving atomic hydrogen or deuterium the deuterium atoms may react faster than the hydrogen atoms due to the difference in zero-point energy at the top of the activation barrier favoring the deuterium atoms. In the initial state since both hydrogen and deuterium are in the atomic form there will be no zero-point energy difference and hence any differences in the activated state will enter in to their full value. It was in the hope that this reaction might furnish an example of this case that this reaction was studied. The other possibility which has to be considered in this connection is that of "tunnelling." If the reduction of mercuric oxide by hydrogen or deuterium atoms is a rate determining step in this reaction one would expect large differences between the rates of the hydrogen and deuterium reaction if tunnelling were an important factor[9] since a deuterium atom will have a very much smaller probability of tunnelling than an atom of hydrogen.

The fact that no such large difference is observed between the rates would indicate that if this is the mechanism then no tunnelling occurs in this particular case.

Assuming a mechanism in which the rate determining process is the reduction of mercuric oxide one is led to an equation for the rate of water formation which qualitatively is in agreement with the experimental facts, and since the quenching efficiencies of hydrogen and deuterium are the same any difference in the rates of reaction will be dependent upon the velocity constant of the reaction $H+HgO \rightarrow HgOH$ or $HgOH+H \rightarrow Hg+H_2O$. This velocity constant will involve the collision frequency between atomic hydrogen or deuterium and the reacting mercuric oxide or hydroxide and whether we imagine this reaction to occur in the vapor phase or on the solid surface of mercuric oxide formed on the walls of the vessel or on the surface of the liquid mercury present, we should expect a difference in collision frequency between hydrogen and deuterium. On the kinetic theory basis the hydrogen should react faster than the deuterium atoms in approximately the ratio of 1.4 : 1. The observed results indicate that hydrogen reacts faster than deuterium in the ratio of 1.05 : 1. This may imply that the simple mechanism we have advanced is not operative in this work or on the other hand that the discrepancy may be due to a smaller activation energy for the deuterium atom reaction because of a smaller zero-point energy of the deuterium in the activated state. This difference would imply an activation energy for deuterium of ~ 200 calories smaller than that for the hydrogen and such a difference could not be detected in the calculation of activation energy over the limited temperature range of this work.

There is, however, the possibility that the hydrogen atoms would rarely react as hydrogen atoms and that because of the high concentration of oxygen molecules would form HO_2 complexes and that the reduction would be carried on by these molecules.

$$HgO+HO_2 \rightarrow HgOH+O_2,$$
$$HgOH+HO_2 \rightarrow Hg+H_2O+O_2.$$

This mechanism would lead to an equation for the rate of reaction which would be formally the same as that for reduction by hydrogen atoms alone. But if the velocity constant of the reduction reaction entered into the equation we would expect a difference in the rate of reaction when hydrogen and deuterium were compared. This difference would arise because the breaking of the $H-O_2$ or $D-O_2$ bond is involved and since this reduction is suspected of being a surface reaction the HO_2 or DO_2 would have suffered stabilizing collisions by the time the complex reached the mercuric oxide and we would suppose that the full zero-point energy would enter into the activation energies.

Since this communication was written a letter has appeared in *Nature* by Melville[10] in which he gives results which are in agreement with the results discussed here. He finds, however, a decrease in the rate of reaction with deuterium as

[8] Polanyi, Nature **132**, 819 (1933).
[9] Bawn and Ogden, Trans. Faraday Soc. **30**, 432 (1934).
[10] Melville, Nature **133**, 947 (1934).

compared with hydrogen at high oxygen concentration. This difference he attributes to a difference in the quenching efficiencies of hydrogen and deuterium. The author is of the opinion that there is no difference in the quenching efficiencies of hydrogen and deuterium.[4] The results reported by Melville would be explained if, at high oxygen concentration, the hydrogen atoms did not take part in the reaction as such but formed relatively stable HO_2 complexes which took part in the subsequent changes. The difference in zero-point energy between the HO_2 and DO_2 would then be more than adequate to account for the changes observed at high oxygen concentration.

This reaction is probably too complex for any simple mechanism to represent the experimental results fully and the most that can be said with certainty is that since there is no great difference observed in the rates of reactions of hydrogen and deuterium the process is either one in which the breaking of a H−X bond does not enter in as a rate determining step or that the reaction is governed by a step involving hydrogen atoms which we would expect from the considerations discussed above to show little or no difference when deuterium is substituted for hydrogen.

The author wishes to thank Professor Hugh S. Taylor for his interest in this work and for the benefit of many helpful discussions, and also for the great facilities afforded the author in these laboratories.

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A Kinetic Expression for the Rate of the Photosensitized Decomposition of Ammonia and Deuteroammonia

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A kinetic expression for mercury sensitized ammonia and deuteroammonia decompositions which represents the experimental data is developed empirically and an explanation of the expression in terms of the various kinetic processes is sought. This expression is further modified to include the intrinsic decomposition probability of the ammonia or deuteroammonia molecule. The final expression is able to express the results quantitatively, and yields values for the quenching ratio, $k_{1NH_3} : k_{1ND_3} = 4 : 1$ and a decomposition probability after quenching $\varphi_{NH_3} : \varphi_{ND_3} = 5 : 1$.

JUNGERS and Taylor[1] have, in a recent publication, discussed the kinetics of the decomposition of ammonia and deuteroammonia on the basis of a kinetic expression derived by Dickinson and Mitchell[2] and Melville.[3] An examination of the experimental results does not lead to a quantitative agreement with the kinetic expression

$$\frac{1}{R}=\frac{1}{K}\left\{1+\frac{k_2[H_2]+k_3}{k_1[NH_3]}\right\}, \qquad (1)$$

where K is proportional to the intensity of the incident light and to the mercury vapor pressure, k_2 and k_1 are the quenching collision factors for hydrogen and ammonia, respectively, and k_3 is the factor for spontaneous loss of energy of excitation of mercury in the $^3P_1$ state.

The discrepancies which arose in the application of the above expression to the experimental data were: (1) a comparison of the quenching efficiencies of ammonia and deuteroammonia obtained from a comparison of the values of k_3/k_1 in the two cases led to a ratio $k_{1(NH_3)} : k_{1(ND_3)} = 4.2 : 1$. If, however, the expression for the hydrogen or deuterium pressure required to reduce the reaction rate to one-half of its initial value were used *viz.*, $k_{2[H_2]\frac{1}{2}} = k_{1[NH_3]} + k_3$ a comparison of $k_{1(NH_3)}/k_{2(H_2)} : k_{1(ND_3)}/k_{2(D_2)}$ led to a ratio of approximately 7 : 1. This would ap-

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[1] Jungers and Taylor, J. Chem. Phys. **2**, 373 (1934).
[2] Dickinson and Mitchell, J. Am. Chem. Soc. **49**, 1487 (1927).
[3] Melville, Proc. Roy. Soc. **A138**, 384 (1932); Trans. Far. Soc. **28**, 805 (1932).

parently mean that, to bring the ratios of $k_{1(NH_3)} : k_{2(ND_3)}$ into agreement, deuterium should be approximately twice as efficient as hydrogen in quenching excited mercury. This, however, has not been found experimentally[4] to be the case and we are, therefore, led to examine the kinetic expression used.

It was possible from the experimental data to plot $1/R$ against $1/NH_3$ or $1/ND_3$ for different constant values of hydrogen or deuterium pressure; this should lead to a series of straight lines with increasing slope as the hydrogen or deuterium concentration is increased, all cutting the $1/R$ axis at the constant value of $1/K$. This however was found not to be the case; a series of straight lines were obtained which did not meet at the intercept of $1/K$ but intersected at a definite value of $1/NH_3$ approximately 0.017 mm^{-1}. This would lead to an empirical expression of the form

$$\frac{1}{R}=\frac{1}{K}\left\{1+\frac{k_2[H_2]+k_3}{k_1}\left(\frac{1}{NH_3}-x\right)\right\}. \quad (2)$$

It was interesting and significant that the empirical value of x for the ammonia and the deuteroammonia data was the same. If this expression is used to determine the ratio of $k_{1(NH_3)}/k_{2(H_2)} : k_{1(ND_3)}/k_{2(D_2)}$ the value obtained is approximately 4 : 1 and agrees well with the ratio of $k_1(NH_3) : k_1(ND_3)$ of 4.2 : 1 obtained from the k_1/k_3 ratio and, moreover, would indicate that the quenching efficiencies of the hydrogen and the deuterium are approximately the same, as found experimentally.[4] The introduction of this empirical correction into the expression for the hydrogen or deuterium pressure at the half reaction rate naturally gives the same result for the above ratio; but, it is also significant that whereas the uncorrected expression gave on plotting $[H_2]_{\frac{1}{2}}$ or $[D_2]_{\frac{1}{2}}$ against NH_3 or ND_3, a curve which was convex to the NH_3 or ND_3 axis and which led to a large amount of uncertainty in the value of k_1/k_2, the corrected expression gives a straight line.

It is of interest to speculate on the theoretical significance of this empirical equation. The experimental results can be represented by a slightly modified form of the empirical equation

$$\frac{1}{R}=\frac{1}{K}\left\{1+\frac{k_2[H_2]+k_3}{k_1[NH_3](1+x[NH_3])}\right\}. \quad (3)$$

This equation yields results which are in agreement with those given above. Expressing the significance of these empirical equations in words one can say that the rate of the photosensitized decomposition of ammonia increases more rapidly with increasing ammonia pressure than is indicated by the expression (1) derived from the simpler kinetic considerations. At small ammonia pressures, the kinetic expression (1) is applicable since the $[NH_3]$ is small compared with unity and the two equations, kinetic and empirical, reduce to the same form. It is only when working at higher pressures, which were enforced in the case of deuteroammonia because of the slow rate of decomposition, that deviations from the kinetic expression are encountered.

We believe that the deviations which are made manifest at these higher pressures are a consequence of the broadening of the absorption line of the mercury vapor. Jablonski[5] has discussed the Lorentz broadening[6] on the basis of the Franck-Condon principle. He assumed that a "quasi" molecule was formed between the absorbing atom and the foreign gas, in this case mercury and ammonia. This complex was held together by van der Waals forces and was capable of absorbing energy from the incident radiation and passing into a complex of excited atom plus foreign gas molecule. Further advances which have been made have employed the London theory of van der Waals forces to define the potential energy curves for the two quasi species. If now we consider the fate of such a complex of an excited mercury atom and an ammonia or deuteroammonia molecule such as will exist in the experiments which we are considering, there are several possibilities. The complex $[Hg'NH_3]$ may spontaneously radiate and fall back again to the unexcited state, the energy of excitation may be transferred to the ammonia molecule which would constitute a quenching process and lastly the complex may

[4] Evans, J. Chem. Phys. **2**, 445 (1934).

[5] Jablonski, Zeits. f. Physik **70**, 723 (1931).

[6] For a discussion of this see Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, p. 158, Macmillan, 1934.

suffer a collision with another ammonia molecule and transfer of energy with or without subsequent decomposition may result. The effect of such complex formation will be to add an extra term to the terms representing the quenching effect of the ammonia, that due to direct quenching being $k_1[NH_3][Hg']$, while that due to the "quenching" of a complex by the ammonia being $k_1x[NH_3]^2[Hg']$. The factor x will depend upon the probability of such complex formation as we have discussed and since only van der Waals forces or polarization forces are operative in the formation of these complexes we should not expect a large difference in the value of x for ammonia and for deuteroammonia again in agreement with the empirical analysis. It is obvious that the introduction of the term $[Hg']k_1[NH_3](1+x[NH_3])$ into the kinetic expressions instead of the simple quenching term $k_1[NH_3][Hg']$ will lead to a kinetic equation of the same form as that obtained empirically. It is not surprising that the $Hg'NH_3$ complex should be quenched by collision with another NH_3 molecule since there will probably be very close resonance between the two. It would appear that the chance of the complex being quenched by hydrogen molecules is comparatively small compared with the ammonia quenching process. In the Jungers-Taylor experiments this is doubly true owing to the relatively small concentrations of hydrogen or deuterium present. In experiments at low ammonia pressures the hydrogen concentration may well become important (cf. reference 2). There is a further discrepancy between the theoretical expression and the experimental results in the value of K. This constant should, from the theoretical equation, be dependent only upon the mercury vapor pressure and on the intensity of the incident radiation. This would imply that the value of K should be the same for the photosensitized decomposition of ammonia and deuteroammonia carried out under the same experimental conditions of mercury vapor pressure and light intensity. In other words, from the kinetic expression, one would expect that, at a sufficiently high ammonia or deuteroammonia pressure, the rates of decomposition of the two should be the same and the value of the initial rate R_0 should be proportional only to the mercury vapor pressure and to the light intensity. This, however, is not found to be the case; when ammonia and deuteroammonia are compared the ratio of the $K_{NH_3} : K_{ND_3}$ is approximately 5 : 1.

We consider that this deviation from the kinetic expression is due to the fact that, in the derivation of this equation, it is assumed that every quenching collision leads to decomposition. This is not necessarily the case and in addition to a difference between ammonia and deuteroammonia in the quenching of excited mercury, there will also be a difference in the probabilities of decomposition of the ammonia and deuteroammonia molecules which have received the energy of excitation from the mercury. An example of this difference is shown in the ultraviolet absorption spectra of ammonia and deuteroammonia; whereas ammonia shows no fine structure in the principal absorption band, deuteroammonia shows discrete levels, the deuteroammonia being stable when the ammonia is predissociating.[7]

If we introduce then a factor φ representing the probability of decomposition of an energy-rich ammonia molecule, the kinetic expression becomes:

$$\frac{1}{R}=\frac{1}{\varphi K}\left\{1+\frac{k_2[H_2]+k_3}{k_1NH_3(1+\kappa NH_3)}\right\}.$$

φ is found to be 5 times greater for ammonia than for deuteroammonia at constant K, a difference which one is inclined to attribute to the difference in zero point energy between the N−H and the N−D bond.

[7] For this information the authors are indebted to Dr. Benedict in this laboratory.

"Isotopic Equilibria" in the Hydrogen-Hydrogen Oxide System

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Experiments are described in which the distribution of deuterium between hydrogen and water vapor at equilibrium at 800°K is investigated. The equilibrium constants of the reactions necessary to describe the system H_2, HD, D_2, H_2O, HDO and D_2O are calculated and the amount of each constituent calculated for various concentrations of deuterium. The distribution of deuterium between the hydrogen and the water is calculated and found to agree with the experimental data.

THE isotopic effect upon equilibrium constants of reactions involving diatomic molecules can be evaluated with precision. The necessary data are the energy levels of the molecules. H. C. Urey and D. Rittenberg[1] investigated the hydrogen iodide equilibrium and were able to predict the experimental results very satisfactorily.

In this research we have investigated a similar exchange reaction in which polyatomic molecules are involved. The energy levels of polyatomic molecules have not been established with nearly the same precision. Mecke and his collaborators[2] have secured the vibration frequencies and moments of inertia of the H_2O molecule and Topley and Eyring[3] have calculated the fundamental vibration frequencies and moments of inertia of the HDO and D_2O molecules, using the theory of Cross and Van Vleck.[4] The degree of precision is high enough so that the free energies can be calculated.

That an isotopic exchange takes place between water and hydrogen was first demonstrated by us[5] and some experimental values of the equilibrium constant for the reaction

$$HDO+H_2\rightleftarrows HD+H_2O$$

at high temperature were presented in a preliminary notice.[6] Other workers[7] have examined the isotope equilibrium at low temperatures in the presence of catalysts. We have studied the equilibrium system involving the six constituents, H_2, HD, D_2, H_2O, HDO and D_2O.

THEORETICAL

As we will show later, if the total concentration of deuterium is less than about 4 percent we can neglect the constituents D_2 and D_2O while if it is above about 96 percent we can neglect the concentrations of H_2 and H_2O. Consequently below 4 percent the only reaction involved is

$$H_2+HDO\rightleftarrows HD+H_2O$$

while above 96 percent we need concern ourselves only with the reaction

$$D_2+HDO\rightleftarrows HD+D_2O.$$

In these ranges of concentration, experiment will give satisfactory values for the equilibrium constants. At intermediate concentrations, however, all constituents must be considered giving the following equilibria:

$$\begin{gathered}H_2+D_2\rightleftarrows 2HD,\\ H_2+HDO\rightleftarrows HD+H_2O,\\ H_2+D_2O\rightleftarrows H_2O+D_2,\\ H_2+D_2O\rightleftarrows HD+HDO,\\ HD+D_2O\rightleftarrows D_2+HDO,\\ H_2O+D_2O\rightleftarrows 2HDO,\\ HD+HDO\rightleftarrows H_2O+D_2.\end{gathered}$$

By appropriate operations these can be reduced to three equations which involve all the components, namely:

$$\begin{aligned}&(1)\quad H_2+D_2\rightleftarrows 2HD,\\ &(2)\quad D_2O+H_2\rightleftarrows H_2O+D_2,\\ &(3)\quad H_2+HDO\rightleftarrows HD+H_2O.\end{aligned}$$

[1] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Rittenberg and Urey J. Am. Chem. Soc. **56**, 1885 (1934).
[2] Mecke, Baumann and Freudenberg, Zeits. f. Physik **81**, 313, 445, 465 (1933).
[3] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
[4] Cross and Van Vleck, J. Chem. Phys. **1**, 357 (1933).
[5] Crist and Dalin, J. Chem. Phys. **1**, 677 (1933).
[6] Crist and Dalin, J. Chem. Phys. **2**, 442, 548 (1934).
[7] K. F. Bonhoeffer, Zeits. f. Elektrochemie **40**, 469 (1934). A. Farkas and L. Farkas, J. Chem. Phys. **2**, 468 (1934).

By appropriate combinations of these equations all the others can be obtained. This particular set was selected because the equilibrium constant of the first has been well established by theory and experiment,[8] and the third can be obtained directly by experiment at low concentrations of deuterium. The second equation is then required to complete the set.

It is possible to write three supplementary equations which contain the six components. These equations are

$$[H_2]+[HD]+[D_2]=100,$$
$$[H_2O]+[HDO]+[D_2O]=100,$$
$$[HD]+2[D_2]+[HDO]+2[D_2O]=2n.$$

The first two result from the experimental condition of equimolecular proportions for the hydrogens and the oxides, the setting of each equal to 100 being arbitrary. In the third equation (n) is taken as twice the total deuterium percentage. We have then the equations

$$\frac{b^2}{ac}=K_1 \quad (3.83), \quad (1) \qquad a+b+c=100, \quad (4)$$

$$\frac{dc}{af}=K_2 \quad (0.61), \quad (2) \qquad d+e+f=100, \quad (5)$$

$$\frac{bd}{ae}=K_3 \quad (0.79), \quad (3) \qquad b+2c+e+2f=2n. \quad (6)$$

where $[H_2]=a$; $[HD]=b$; $[D_2]=c$; $[H_2O]=d$; $[HDO]=e$; $[D_2O]=f$.

In order to calculate the equilibrium constant[9] of (2) we use

$$K_2=(f_{H_2O}\cdot f_{D_2})/(f_{D_2O}\cdot f_{H_2}),$$

where the distribution functions for H_2O and D_2 are

$$f_{H_2O}=\left[\exp-\frac{E_d}{kT}\right]\frac{[2\pi m_d kT]^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2[8\pi^3(ABC)_d]^{\frac{1}{2}}}{2h^3}$$
$$\times(kT)^{\frac{3}{2}}\prod_{i=j,\,k,\,l}\frac{1}{1-\exp(-h\nu_i/kT)}\times 4,$$

$$f_{D_2}=\left[\exp-\frac{E_c}{kT}\right]\frac{[2\pi m_c kT]^{\frac{3}{2}}}{h^3}\sum_{v,\,j}p\exp\left(\frac{-E_{v,\,j}}{kT}\right).$$

ABC are the three moments of inertia, E is the zero point energy, h and k have their usual significance. The functions for D_2O and H_2 are similar except that the statistical factor for D_2O is 9. The equilibrium constant is given by

$$K_2=\exp\left[\frac{E_a+E_f-E_c-E_d}{kT}\right]\left[\frac{m_d m_c}{m_f m_a}\right]^{\frac{3}{2}}$$
$$\times\left[\frac{(ABC)_d}{(ABC)_f}\right]^{\frac{1}{2}}\frac{\Pi_d}{\Pi_f}\frac{Q_c}{Q_a}\times\frac{4}{9}.$$

The data for the Q's were obtained from the work of Urey and Rittenberg,[10] and of Johnston and Long.[11] The other necessary data were obtained from Topley and Eyring's work. The values of K_2 for 373°K and 800°K are 0.2 and 0.606, respectively, while those for K_3 are 0.48 and 0.79. Additional values are given in the preliminary note referred to above. The low temperature values compare favorably with the results of Bonhoeffer and of Farkas.[12]

By appropriate substitutions in Eqs. (1)–(6) we find the equations:

$$e^2=(K_1K_2/K_3^2)d(100-e-d), \qquad (7)$$

TABLE I.

%D in total system	$H_2(a)$	$HD(b)$	$D_2(c)$	$H_2O(d)$	$HDO(e)$	$D_2O(f)$	$\frac{a}{\beta}$
			Temperature = 800°K				
0	100	0	0	100	0	0	—
10	82.00	16.12	0.8265	79.13	19.57	1.30	0.81
30	52.91	39.42	7.68	45.77	43.23	11.00	.84
50	28.46	49.32	22.22	22.38	48.99	28.62	.88
70	10.94	43.58	45.48	7.723	39.09	53.18	.93
90	1.28	19.81	78.91	0.8253	15.97	83.20	.97
100	0	0	100	0	0	100	—
			Temperature = 373°K				
0	100	0	0	100	0	0	—
30	61.84	33.05	5.11	39.61	44.05	16.34	0.56
50	37.41	46.08	16.50	17.30	44.49	38.21	.65
70	16.11	45.57	38.23	5.25	31.50	63.24	.77
100	0	0	100	0	0	100	—

$\alpha=\frac{b+2c}{2(a+b+c)}$, the deuterium percentage in the hydrogen.

$\beta=\frac{e+2f}{2(d+e+f)}$, the deuterium percentage in the water.

[8] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Rittenberg, Bleakney and Urey, J. Chem. Phys. **2**, 48 (1934). A. Farkas and L. Farkas, Nature **132**, 894 (1933); Proc. Roy. Soc. **A144**, 467 (1934).

[9] See Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

[10] Reference 8.

[11] H. L. Johnston, and E. A. Long, J. Chem. Phys. **2**, 389 (1934).

[12] Reference 7.

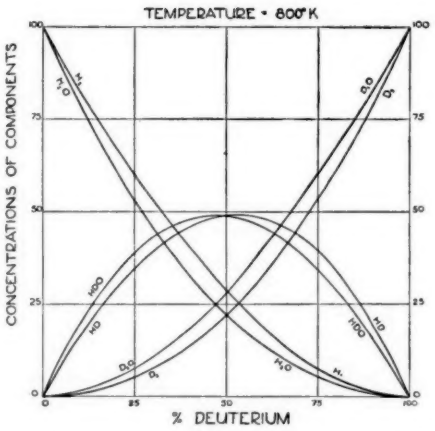

FIG. 1. Equilibrium concentrations of hydrogen-hydrogen oxide systems. Temperature = 800°K. The ordinate represents the concentration of the components on the basis of 200 (see Eqs. (4) and (5)).

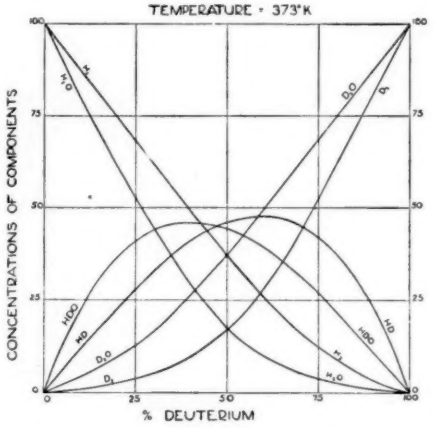

FIG. 2. Equilibrium concentrations for temperature of 373°K.

$$[K_1d+2K_3e]100\cdot K_3e+[200-e-2d-2n]\times[K_1d^2+K_1K_3de+K_3^2e^2]=0, \quad (8)$$

$$c=\frac{100K_3^2e^2}{K_1d^2+K_1K_3de+K_3^2e^2}. \quad (9)$$

The values of the constants given in (1), (2) and (3) in parenthesis are for 800°K and are used in the calculations that follow. Eqs. (7) and (8) were solved for different values of n. The concentrations of all the components can then be obtained from Eqs. (9), (4), (5) and (6). The results of the calculations are given in Table I and Figs. 1 and 2. In Fig. 2 are the results of the calculation for 373°C.

EXPERIMENTAL

The experiments were carried out in a Pyrex tube of 1565 cc capacity. This was sealed inside a larger tube containing boiling sulfur. The boiling point of the sulfur was controlled by maintaining a constant pressure of nitrogen over the sulfur. This was accomplished by means of a regulated heater in an auxiliary flask, the necessary contacts being made on a manometer.[13] A thermocouple calibrated with a type K potentiometer against boiling sulfur at atmospheric pressure, and against the freezing point of antimony gave the temperature of the reaction vessel within 0.5°C. The variation in temperature over the inner tube of the reaction vessel was less than 0.5°C and no variation with time was discernible. Platinum foil was put in the reaction vessel to catalyze the reaction. The water was first distilled into the vessel which was then filled with hydrogen to a pressure of 657 mm at 25°C. Deuterium rich hydrogen was prepared by passing water vapor over sodium, with continuous operation of a Toepler pump to remove the hydrogen produced. The

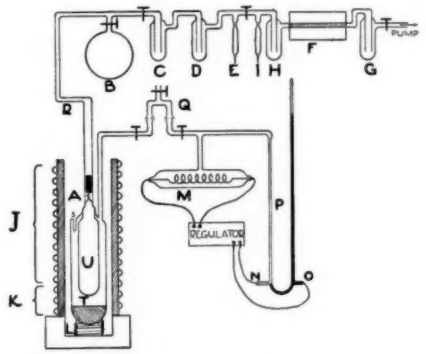

FIG. 3. When the breakseal A is broken by the plunger above it, the gas expands into the five liter flask B. The water is trapped out in C and D and later distilled into E which is sealed off and removed for measurement. The hydrogen is slowly passed over the copper oxide in the furnace F and the water formed trapped in G. Trap H prevents any back distillation of the water formed in F. This water is later distilled into I and removed. Coils J, K and L, wound on asbestos, are separately regulated to avoid superheating of the sulphur vapor T surrounding the reaction vessel U. Bulb M contains the heater which keeps the pressure constant. N and O are the metal contacts on the manometer P. Removing the cap Q and breaking the tube R makes it possible to shift the reaction vessel so that it can be immersed in dry ice and water distilled into it. S is a well for a thermocouple.

[13] C. C. Coffin, J. Am. Chem. Soc. **55**, 3646 (1933).

reaction vessel was then heated in a furnace, 1½ hours being required to come up to temperature. Trial showed that the reaction was about two-thirds complete in two hours and all runs thereafter were over eighteen hours in length. The exception is Experiment 4 where the original mixture was almost in the equilibrium proportions and the time was ten hours. At the end of the run the gases were withdrawn through a break seal while the reaction vessel was kept at the original temperature. The water was removed and the hydrogens were passed over hot copper oxide. The recovery of hydrogen and water was complete as was shown by weighing the separate fractions. The samples of water were analyzed with the interferometer as described previously.[14] The final analyses were taken to represent the equilibrium concentrations. The results are given in Table II. (See Fig. 3 for a description of the apparatus.)

TABLE II. *Experimental equilibrium data.*

No.	Time in hours	α	β	$\frac{\alpha}{\beta}$ exp.	$\frac{\alpha}{\beta}$ calc.
1*	42	2.36	3.02	0.784	0.79
2*	18	3.124	3.928	.794	.79
3*	38	2.93	3.82	.767	.79
4	10	30.19	36.74	.823	.85
5*	24	37.77	44.12	.856	.86
6*	48	38.662	44.757	.863	.86
7	27	83.40	88.32	.944	.96

* Ordinary hydrogen at start.
Temperature = 800°K. Catalyst = platinum except (1) where copper was used. In (4) and (7) α and β at the start were about the same. The hydrogen molalities were 66 and 81 percent, respectively, of the water. A simple proof shows (as does actual calculation) that α/β exp. for (4) and (7) is directly comparable with α/β calc. which has been derived for the case where $a+b+c=d+e+f$.

During the course of the work the reaction vessel became considerably darker in color and eventually became almost completely opaque. Measurement of α and β and of the water before it was placed in the reaction vessel showed that a small amount of deuterium disappeared during the course of each run. Table III contains data on the loss of deuterium.

$\Delta\ (\alpha+\beta)$ is roughly proportional to the length of the experiment. It certainly depends on the temperature and we should expect it to depend on the previous history of the vessel. However, the small size of the average deviation of α/β from runs (1), (2) and (3) and from runs (5) and (6) in Table II offers good evidence that α/β is affected but slightly by the loss of deuterium. The average deviation for experiments (1), (2) and (3) is 0.013 and for (5) and (6) is 0.004. The darkening of the vessel was first noticed during some experiments on the kinetics of the reaction $HDO+H_2 \rightleftarrows H_2O+HD$. This indicates a reaction, probably, between the hydrogen and the glass. There is also the possibility of an exchange between the deuterium oxides and the water in the glass. The experiments were run with proper care in the rapid heating of the vessel and rapid cooling so as to avoid large uncertainties in the time of the experiment, but the size of the deuterium loss makes the measurements in Pyrex unreliable for rate studies.

TABLE III.

No.	t	$(\alpha+\beta)_1$	$(\alpha+\beta)_2$	$\frac{\Delta(\alpha+\beta)}{(\alpha+\beta)_1}$	$\frac{\Delta(\alpha+\beta)}{t(\alpha+\beta)_1}\times 10^3$
(1)	42	6.25	5.38	0.139	3.31
(2)	18	7.33	7.05	.0382	2.12
(3)	38	7.33	6.75	.0792	2.08
(5)	24	85.213	81.89	.0389	1.62
(8)	43	85.213	84.325	.0104	0.243

t = time in hours. $(\alpha+\beta)_1$ = conc. of deuterium before being placed in furnace. $(\alpha+\beta)_2$ = conc. of deuterium after being placed in furnace. Expt. 8 = Blank run with water alone.

The experiments yield the ratio of the deuterium in the hydrogen components to that in the oxide components. With low concentrations of deuterium the four components concerned can be calculated readily and the equilibrium constant obtained. However, at high concentrations it is necessary to compare the ratio to that calculated from the equilibrium concentrations in Table I. The calculated values are given in the last column of Table II. The correspondence with the experimental ratios is satisfactory.

The authors are indebted to Professor H. C. Urey for valuable advice and for the heavy water used, and to Dr. D. Rittenberg for helpful discussions during the course of the work.

[14] Crist, Murphy and Urey, J. Chem. Phys. **2**, 112 (1934).

The Photochemical Oxidation of Phosphine above the Upper Explosion Limit

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An investigation has been made of the kinetics of the photochemical oxidation of phosphine above the upper explosion limit. The results are summarized by the equations

Mercury sensitized reaction $-d[PH_3]/dt = \text{const.}\ [PH_3]/[O_2]^2 \times \text{intensity}.$

Direct photo-reaction $-d[PH_3]/dt = \text{const.}\ [PH_3]^2/[O_2]^2.$

The reactions are shown to be of the chain type and inhibited by oxygen. On the basis of previous knowledge of the propagation of the chains, the question of termination was examined and it is shown that out of six possible cases, only one is in agreement with the experimental facts. This is that the chain carrier, which normally reacts with phosphine, is destroyed in a ternary collision with two oxygen molecules or with one oxygen and one nitrogen molecule (or an argon atom). The efficiency of the collision is about 0.5. In view of these results, it is highly probable that this carrier is an oxygen atom. In the photosensitized reaction one-fifth of the collisions between oxygen molecules and excited mercury atoms results in the initiation of a chain. These results are shown to be quantitatively consistent with the shape and also the position of the upper limiting explosion curve, except that the limiting pressure is a little higher than that calculated by a strict application of the theory of branched chains. The upper limit is displaced to higher pressures by illumination of the mixture, a phenomenon not predicted by theory. The effect is of short duration, <2 sec. and it is not exhibited at the lower limit. The significance of this result is discussed in relation to the theory of the reaction.

THE introduction of the conception of branching chains and of the diffusion of chain carriers to the walls into the theory of thermal chain reactions has provided an acceptable picture of the mechanism of many oxidation reactions. While much experimental work has revealed the essential similarity underlying these reactions there are many corollaries to the theory which have yet to be explored in detail. The difficulty, in many cases, is experimental; in others, it is not at present quite certain whether factors not at all included in the chain theory prevent to some extent its rigorous application. For example, there is a possibility that sharp explosion limits may be due to causes other than simple branching of the reaction chains.

One of the corollaries is the following: It is postulated that the condition for explosion is that the product of the probabilities of branching and termination be equal to unity. The limits should consequently be independent of the rate of starting of the chains, provided that there is actually some reaction taking place.

A second is concerned with the mechanism of the reaction outside the explosion limits. In the quantitative application of the theory, expressions are derived which give the stationary concentration of the carriers for any pressure. It happens, however, that in the thermal reaction, the rate of starting is often so small that a stable reaction is never observed. Sometimes, the stable is masked by a relatively fast heterogeneous reaction.

The reaction between phosphine and oxygen is particularly well suited to answer some of these questions. Its mechanism is undoubtedly complicated, but the general chain features which it exhibits are in very good agreement with the theory. Moreover, it has the further advantage that the propagation collisions are nearly one hundred percent efficient and thus do not require any energy of activation.[1] The correlation between the kinetics below and at the lower limit has been fairly fully established.[1, 2] No experiments have, however, been carried out above the upper limit except a preliminary set[3] where a complete analysis was not attempted. Such an analysis was necessary in order to establish a relationship between the two conditions.

In this connection, curious results have been obtained by Grant and Hinshelwood[4] at the upper limit in the hydrogen-oxygen reaction.

* Senior Student, Exhibition of 1851.

[1] Melville, Proc. Roy. Soc. **A139**, 555 (1933).
[2] Dalton and Hinshelwood, Proc. Roy. Soc. **A125**, 294 (1929); Melville, ibid. **A138**, 374 (1932).
[3] Melville and Roxburgh, Nature **131**, 690 (1933).
[4] Grant and Hinshelwood, Proc. Roy. Soc. **A141**, 29 (1933).

The limit is apparently governed by some form of gas phase inhibition, for argon and helium lower the upper explosion pressure. Above the limit, however, there is a stable reaction in which the same gases accelerate the reaction rate showing that the chains now end on the walls. It was thought at first that two entirely different mechanisms were in operation, for obviously, one of the conditions for the appearance of an upper limit is that the chain length should increase with decreasing pressure, whereas the kinetics of the stable reaction indicated that the chain length probably increased with pressure. The explanation apparently is that the decrease in chain length is more than compensated for by the increase in the probability of branching as the pressure is reduced.

It was thought that instead of employing photochemical means of artificially increasing the rate of starting, the introduction of a hot filament might prove just as suitable and at the same time provide detailed information about the heterogeneous starting of chain reactions. Unfortunately, the reaction is almost wholly heterogeneous[5] and so photo-initiation had to be employed.

The Theory of the Stable Reactions

The theory has been worked out for the kinetics at the explosion limits[6] but to apply it to the stable reactions requires some modification. Before deriving the equations for a number of assumptions, it is necessary to examine the simplifications which were made in the original theory. It was assumed that both carriers X_O and X_P are equally well removed by collision with the walls and that the rates of reaction with phosphine and with oxygen, respectively, are the same. There is a considerable amount of evidence that these assumptions are sufficiently exact for the purposes of calculation. For example, the theoretical and observed chain lengths below the lower limit are in good agreement, and the second postulate must be nearly true. If one carrier were more easily destroyed than the other, then it can easily be shown that the lower explosion limit equation would be

$$[PH_3]\{[PH_3]+[O_2]\}=\text{const.} \quad (1)$$

or

$$[O_2]\{[PH_3]+[O_2]\}=\text{const.}, \quad (2)$$

which is not in so good accordance with experiment as the equation $[PH_3][O_2]=\text{const.}$ Below the lower limit, the stationary concentrations of the carriers are given by

$$d[X_O]/dt = I + k[X_P][O_2] + k[X_O][PH_3] - K[X_O] = 0, \quad (3)$$

$$d[X_P]/dt = k[X_O][PH_3] - k[X_P][O_2] - K[X_P] = 0 \quad (4)$$

and therefore

$$-d[PH_3]/dt = (k[PH_3][O_2]/K') \cdot I, \quad (5)$$

where $K=K'/([PH_3]+[O_2])$, K being a constant and I the rate of starting.

Above the upper limit, there are a number of ways in which X_O and X_P may be destroyed. One of the objects of this investigation is to determine the kinetics of the reaction in order that an unequivocal choice may be made from among the possible mechanisms, and further to see whether the mechanism so chosen is consistent simultaneously with the position and shape of the upper limit curve.

There are six possible ways whereby the carriers could be destroyed

1. X_O+X (k_4), 4. X_P+X (k_7),
2. X_O+X_O+X (k_5), 5. X_P+X_P+X (k_8),
3. X_O+X+X (k_6), 6. X_P+X+X (k_9).

k is the velocity coefficient and X is either PH_3 or O_2 or any other molecule which may have been added to the gas mixture. Three examples of each case will be worked out *viz.*, (*a*) mercury sensitized initiation; in addition to the dissociation of the PH_3 by $Hg(^3P_1)$, it may also happen that oxygen is activated in such a manner as to start chains, and there are therefore two equations for this kind of initiation, (*b*) direct photo-dissociation of the PH_3.

This procedure of examining each possibility is adopted in order to meet a criticism which is often advanced against the interpretation of kinetic results, namely, that two or more mechanisms may lead to the same equation. This occurs, in fact, in the present analysis, but fortunately there are means by which an unambiguous choice can be made.

[5] Melville and Roxburgh, J. Chem. Soc. 586 (1933); 264 (1934).

[6] See, e.g., Hinshelwood, *Kinetics*, 3rd edition, p. 264.

Case 1

The equations for $[X_O]$ and $[X_P]$ are

$$d[X_O]/dt = I + k[X_P][O_2] - k[X_O][PH_3] - k_4[X_O][X] = 0, \tag{6}$$

$$d[X_P]/dt = k[X_O][PH_3] - k[X_P][O_2] = 0. \tag{7}$$

For the mercury sensitized reaction, phosphine being dissociated

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n[PH_3]}{[PH_3]+0.5[O_2]+0.37}. \tag{8}$$

The constant 0.37 (allowing for the radiation of resonance light) is calculated for the case where $[PH_3]$ and $[O_2]$ are expressed in mm of mercury, for a 2 cm tube and a mercury vapor pressure of 0.001 mm,[7] I_n is proportional to the intensity of the 253.7 mμ line from the mercury lamp. One important simplification can now be made. In the region above the upper limit where the phosphine pressure is low, that of the oxygen is so high that X in the above reaction scheme may be considered to be O_2. Eq. (8) can thus be simplified to

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2]^2) \cdot I_n. \tag{9}$$

For mercury sensitization with initiation by oxygen,

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n \cdot \{A \cdot [O_2] \cdot 0.5 + [PH_3]\}}{[PH_3]+0.5[O_2]+0.37} = \frac{k[PH_3]}{k_4[O_2]} \cdot I_n, \tag{10}$$

where A is defined as the number of chains started per excited mercury atom which is deactivated by oxygen. For the direct dissociation,

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2])I_n. \tag{11}$$

Case 2

The last term in the equation for X_O will now be $-k_5[X_O]^2[X]$ and therefore

$$I = k_5[X_O]^2[X]. \tag{12}$$

Mercury sensitization (PH_3)

$$-\frac{d[PH_3]}{dt} = k[PH_3]\left\{\frac{[PH_3] \cdot I_n}{k_5[X]([PH_3]+0.5[O_2]+0.37)}\right\}^{\frac{1}{2}} = \frac{k[PH_3]^{\frac{3}{2}}}{[O_2]}\left(\frac{I_n}{k_5}\right)^{\frac{1}{2}}. \tag{13}$$

Mercury sensitization (O_2)

$$-d[PH_3]/dt = k[PH_3](I_n \cdot A/k_5[O_2])^{\frac{1}{2}}, \tag{14}$$

and the direct reaction

$$-d[PH_3]/dt = k[PH_3]^{\frac{3}{2}}(I_n/k_5[O_2])^{\frac{1}{2}}. \tag{15}$$

Case 3

The last term in the equation for $[X_O]$ is $k_6[X_O][X]^2$. Mercury sensitization (PH_3),

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_6[X]^2} \cdot \frac{[PH_3] \cdot I_n}{[PH_3]+0.5[O_2]+0.37} = \frac{k[PH_3]^2 \cdot I_n}{k_6[O_2]^3}. \tag{16}$$

Mercury sensitization (O_2),

$$-d[PH_3]/dt = (k[PH_3]I_n \cdot A)/k_6[O_2]^2. \tag{17}$$

Direct reaction,

$$-d[PH_3]/dt = (k[PH_3]^2 \cdot I_n)/k_6[O_2]^2. \tag{18}$$

[7] Cf. Proc. Roy. Soc. **A138**, 385 (1932).

Cases 4, 5 and 6

The corresponding cases for X_P are obtained in exactly the same way. The last term in the X_O equation is discarded, while an additional term is added to the X_P equation in order to express how this carrier is removed. This gives rise to the following nine equations.

$$\text{Case 4}\quad X_P+X \quad (k_7)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt = kI_n/k_7, & (19)\\ \text{Hg } (O_2) & -d[PH_3]/dt = k[O_2]\cdot A/k_7[PH_3], & (20)\\ \text{Direct} & -d[PH_3]/dt = k[O_2]/k_7. & (21)\end{cases}$$

$$\text{Case 5}\quad X_P+X_P+X \quad (k_8)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt = k([PH_3]\cdot I_n/k_8)^{\frac{1}{2}}, & (22)\\ \text{Hg } (O_2) & -d[PH_3]/dt = k(I_n\cdot A/k_8[O_2])^{\frac{1}{2}}, & (23)\\ \text{Direct} & -d[PH_3]/dt = k([O_2][PH_3]\cdot I_n/k_8)^{\frac{1}{2}}. & (24)\end{cases}$$

$$\text{Case 6}\quad X_P+X+X \quad (k_9)\begin{cases}\text{Hg } (PH_3) & -d[PH_3]/dt = k[PH_3]I_n/k_9[O_2]^2, & (25)\\ \text{Hg } (O_2) & -d[PH_3]/dt = k\cdot[PH_3]\cdot I_n/k_9[O_2], & (26)\\ \text{Direct} & -d[PH_3]/dt = k[PH_3]I_n/k_9[O_2]. & (27)\end{cases}$$

A possible objection might be raised against case 6, for $X=O_2$ and X_P+O_2 is a propagating collision. In presence of a third molecule, however, it is quite conceivable that a redistribution of energy occurs in such a way as to prevent the emergence of an X_O molecule from the collision.

Experimental

Fig. 1 illustrates the essential parts of the apparatus. The main difficulty was to measure a change in phosphine pressure in presence of a large excess of oxygen. The apparatus was so arranged that it could readily be used for experiments on the upper limit. The silica reaction tube was placed in a water bath at 20°C fitted with a silica window. The source of the mercury line was a tungsten anode lamp L with a water-cooled cathode. A filter was employed to vary the intensity of the light and consisted of a solution of carbon tetrachloride in pure hexane.[8] A condensed spark between zinc disks rotating at right angles served as a light source for the experiments on the direct reaction. The input to the spark was about 0.2 amp. at 5000 volts, the distance between spark and reaction tube being 15 cm. Large pressures were measured by a capillary mercury manometer, smaller pressures by the spring gauge M_2 and low pressures by the oil manometer M_1, the position of the meniscus being read by a microscope. Apiezon oil A, thoroughly degassed, proved to be satisfactory. To increase the sensitivity, one of the limbs was made much wider than the other. Since this manometer was used differentially, it was also placed in a water bath. For the experiments at the upper limit, a steel needle valve was attached to the apparatus to regulate the rate of exhaustion of the explosion tube.

The procedure for the experiments on the stable reaction above the upper limit and at low phosphine pressures was as follows: Phosphine was admitted to R and to M_1, T being closed, and its pressure observed. T was opened and oxygen admitted, the pressure being now measured on

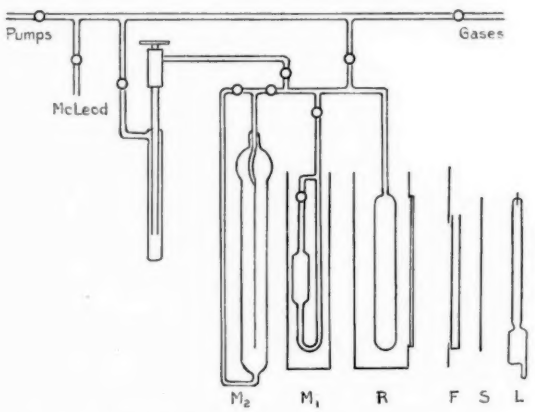

FIG. 1. Diagram showing essential parts of apparatus.

[8] Melville and Walls, Trans. Faraday Soc. **29**, 1255 (1933).

M_2, T was closed again and the shutter removed for a given time, after which the oil manometer was again read. This procedure was repeated for a number of exposures. In this manner, changes of pressure of 0.1 mm could be measured in presence of 30 mm of oxygen. Several blank experiments were made with oxygen alone to ensure that no spurious effects occurred, for instance, oxygen does dissolve in the oil, but since it was present at the same pressure in both limbs of the manometer and the runs were not prolonged, no appreciable change of oil level could be detected. The deposition of the phosphoric acid on the walls of the reaction did not appear to cut down the reaction velocity, for no increase in rate resulted when the tube was cleaned out. With excess of oxygen, the phosphine is practically completely oxidized to H_3PO_4, since the pressure decrease after the reaction had gone to completion amounted to nearly three times the pressure of the phosphine.

The preparation of mixtures above the upper limit was carried out in the usual way. The water bath surrounding the reaction vessel was removed and a small annular cup was fixed to R. Phosphine was passed in, liquid air poured into the cup and then the oxygen was added. When the liquid air had evaporated, the water bath was replaced and the apparatus allowed to stand for a few minutes until the pressure became steady, after which exhaustion and exposure were commenced.

The gases were prepared as described in previous papers.

Results

Photosensitized oxidation

It will be observed from an inspection of Eqs. (13)–(15) and (22)–(24) that the rate of oxidation for cases 2 and 5 should vary as the square root of the intensity, whereas in the other cases the relation is linear. Several possibilities can thus at once be eliminated if the intensity law is first of all investigated. Below the lower limit, the rate should, of course, be proportional to the intensity. The results (Table I) below the lower limit are in accordance with expectation and above the upper limit, there is no doubt that the rate is proportional to the first power of the intensity and therefore cases 2 and 5 may at once be eliminated. For a given pressure of phosphine, it is known from the experiments of Dalton and others[9] that by increasing the pressure of oxygen, the lower limit may be approached, or if the oxygen pressure be decreased, the upper limit is reached. The upper limit must, therefore, be due to oxygen participating in some reaction which is negligible at low pressures. When chain initiation is brought about by mercury sensitization, it is probable that oxygen molecules account for a number of the chains started and it is therefore necessary to evaluate the magnitude of the coefficient A defined on p. 741. In Fig. 2, $1/R$ and k^{-1} have been plotted against p_{O_2}, the dotted curve refers to the ideal case in which

TABLE I.

Intensity I	Init. Rate R (mm/min.)	R/I^*	t for $\Delta p=0.525$ mm (min.)
Lower limit, $p_{PH_3}=0.254$ mm, $p_{O_2}=0.584$ mm			
1.00	0.072	0.072	0.85
0.15	0.012	0.072	5.20
0.68	0.053	0.072	1.05
0.38	0.028	0.065	2.00
1.00	0.083	0.072	0.70

Intensity	t for $\Delta p=0.064$	$t\times I$
Upper limit, $p_{PH_3}=0.127$ mm, $p_{O_2}=10.0$ mm		
0.38	1.65	0.63
0.68	0.90	0.61
1.00	0.55	0.55
0.15	3.70	0.56
0.51	1.24	0.63

* Corrected for the increase in the intensity during the series.

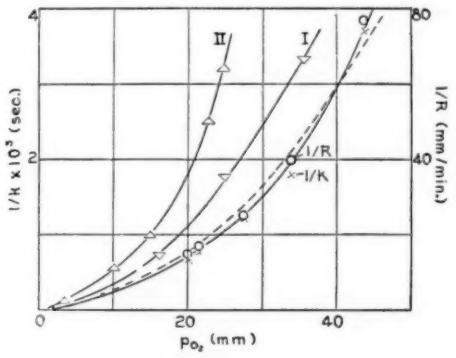

FIG. 2. Photosensitized reaction, curves I and II are for $p_{PH_3}=0.120$ mm and different intensities.

[9] Dalton and others, e.g., Proc. Roy. Soc. **A128**, 263 (1930).

TABLE II.

p_{PH_3}	0.261		0.261		0.261		0.261		0.261	
p_{O_2}	20.0		21.4		27.0		34.0		44.0	
t	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)	Δp	$k\times10^3$ (sec.$^{-1}$)
0.25	0.017	1.54	0.016	1.22	0.009	—	—	—	0.001	—
0.50	0.033	1.41	0.029	1.30	0.021	0.92	0.012	—	—	—
0.75	—	—	.0430	1.23	0.029	0.81	0.017	0.51	—	—
1.00	0.066	1.51	0.055	1.19	0.041	0.92	0.025	0.52	—	—
1.50	0.092	1.40	0.079	1.23	0.056	0.84	0.042	0.61	0.016	—
2.00	0.118	1.73	0.097	1.09	0.073	0.81	0.047	0.54	0.026	0.26
3.00	0.162	1.28	—	—	0.104	0.78	0.071	0.54	0.035	0.26
4.00	—	—	—	—	—	—	0.094	0.54	0.055	0.29

$1/R$ and k vary as $p_{O_2}^2$. Table II contains the detailed runs and k is calculated assuming that $-d[PH_3]/dt=k[PH_3]$. The oxygen pressure may be regarded as constant during the reaction. Since these runs were not carried to completion, another series of experiments is given in Table III, where the pressure of oxygen was maintained

TABLE III. *Effect of phosphine.*

p_{PH_3}	0.260	0.190	0.129	0.132	0.066
p_{O_2}	9.4	10.5	9.2	10.0	10.0
Rate (R)	0.100	0.066	0.051	0.046	0.025
R/p_{PH_3}	0.038	0.035	0.039	0.035	0.038
$t(\Delta p=0.066)$	0.65	1.15	1.55	1.86	2.95
$t\times p_{PH_3}$	0.169	0.22	0.20	0.24	0.20

constant and that of phosphine varied. The constancy of R/p_{PH_3} and of $t\times p_{PH_3}$ shows that the rate is proportional to the pressure of the phosphine.

In Table IV, three series of results are listed for a constant oxygen pressure and for different argon pressures. First of all, it is seen that argon

TABLE IV. *Effect of argon. Hg sensitized reaction.*

p_{PH_3}	p_{O_2}	p_A	R	$\frac{(1/R-1/R_0)}{p_A}$*	t for Δp		k_{10}/k_6
					$=0.039$		
0.260	25.0	55.0	0.0086	1.5	4.50		1.00
0.260	24.6	—	0.0285	—	1.45		—
0.263	25.7	14.6	0.0193	1.3	2.20		0.8
					Δp	Δp	
					$=0.039$	$=0.131$	
0.263	14.9	16.1	0.051	0.52	0.82	3.68	0.8
0.262	15.0	—	0.093	—	0.41	2.00	—
0.258	15.6	26.4	0.033	0.74	1.18	4.60	1.0
0.262	15.5	7.7	0.066	0.57	0.64	3.05	0.8
					$\Delta p=0.0655$		
0.261	14.6	44.9	0.0201	0.82	4.00		0.7
0.262	15.8	16.4	0.0283	1.00	2.47		0.9
0.261	15.8	—	0.0533	—	1.27		—

* R_0 is the rate in absence of inert gas.

inhibits the oxidation, although in comparison with oxygen it does not quench mercury resonance radiation. The inhibition must therefore be due to chain termination and since the value of $(1/R-1/R_0)/p_A$ is approximately constant, the inhibition term in the kinetic equation may be expressed in two ways *viz.*, $k_{10}[X_O][A]$ or $k_{11}[X_O][O_2][X]$.

Similarly, there is inhibition by nitrogen (Table V) and again according to the same law.

TABLE V. *Effect of nitrogen.*

Direct reaction, Zn spark
$p_{PH_3}=0.254$, $p_{O_2}=12$

p_{N_2}	12	26	18	6	0
t for $\Delta p=0.064$	2.62	3.84	3.37	1.62	1.17
k_{10}/k_6	1.2	1.1	1.2	0.80	—

Hg reaction, constant $p_{O_2}+p_{N_2}$

p_{PH_3}	p_{O_2}	p_{N_2}	R	t for $\Delta p=0.131$
0.262	39.0	—	0.066	2.22
0.256	11.0	32.0	0.074	2.16
0.271	20.4	20.3	0.104	1.47
0.259	10.8	30.5	0.131	1.06
0.271	26.7	13.3	0.090	1.75

Until a decision is made about the mechanism of termination, no calculation can be made of the coefficients k_{10} and k_{11}.

The kinetics of the reaction are, therefore, that

$$-d[PH_3]/dt=\text{const. } [PH_3]/[O_2]^2.$$

This does not decide the matter unequivocally, since case 3 and case 6 lead to the same equation if initiation in the first is due to oxygen and in the second to phosphine. Further, both cases allow the introduction of an inhibitory term containing oxygen, and argon and nitrogen. The inhibition by inert gases practically excludes cases 1 and 4

for it is probable, although the evidence is as yet indirect, that the chain carriers are not excited molecules of very short life and hence collision of X_O or X_P with argon or nitrogen should not lead to destruction.

Direct photo-oxidation

The number of mechanisms has now been reduced to two. Fortunately, the kinetic equations for the direct oxidation are quite different for cases 3 and 6 and thus it should be possible to decide which is the more probable. Intensity measurements were not considered to be necessary in view of the definite answer given by the photosensitised experiments. In Table VI the

TABLE VI. *Effect of phosphine.*

p_{PH_3}	p_{O_2}	t for $\Delta p=0.025$ (sec.)	$t\times p_{PH_3}^2$
0.130	17.3	108	18.2
0.535	17.7	7	20.0
0.275	17.4	26	19.7
0.131	17.2	85	14.6
0.391	17.3	10	15.3
0.261	17.3	20	13.6

complete data are given for varying oxygen and phosphine pressures. In Fig. 3, $1/R$ and t for $\Delta p=0.100$ mm have been plotted against $p_{O_2}^2$ and also against p_{O_2}, the pressure of PH_3 being 0.26 mm. The straight line obtained with the $p_{O_2}^2$ plot and also the constancy of the product $t\times p_{PH_3}^2$ in Table VI, indicates that the kinetics in this pressure range can be summarized by the equation,

$$-d[PH_3]/dt=\text{const. } [PH_3]^2/[O_2]^2.$$

Referring back to the theory given above, it will be observed that this equation only agrees with case 3 (18) and therefore the conclusion which may be drawn is that, above the upper limit, the chains are terminated by a triple collision between the chain carrier X_O, which normally reacts with phosphine, and with two oxygen molecules.

It is now possible to return to the question of inhibition by argon and nitrogen. The plots of $1/R$ against $p_{A(N_2)}$ are straight and hence the inhibition term will contain a factor $[N_2]$ or $[A]$. It is of importance to note that a quadratic term $[N_2]^2$ or $[A]^2$ need not be introduced. The most

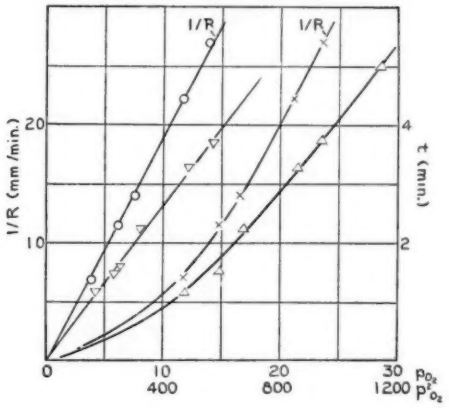

FIG. 3.

probable mechanism of the termination is that X_O must collide with a nitrogen molecule and an oxygen molecule. The function of the inert gas may simply be to stabilize the complex X_O+O_2 and thus prevent X_O further propagating the chain. Let the inhibition term be $k_{10}[O_2][N_2][X_O]$, then k_{10} may be evaluated in the following way. Inserting this term in the equation for X_O in addition to the term required by case three (oxygen initiation)

$$-\frac{d[PH_3]}{dt}=\frac{k[PH_3]I_n\cdot A}{[O_2]\{k_6[O_2]+k_{10}[N_2]\}}.$$

Hence

$$(1/R)/(1/R_0)=1+k_{10}[N_2]/k_6[O_2], \quad (28)$$

where the subscript $_0$ refers to the runs made in absence of foreign gas. From this equation the values of k_{10}/k_6 have been calculated and are given in Tables IV and V. Argon and nitrogen are about as efficient as oxygen in promoting the stability of the complex.

The next question is to determine the absolute values of k_6 and also of A. For this purpose, the ratio of the rates of oxidation to the rate of decomposition for the photosensitized and for the direct reaction were measured. The data are collected in Table VII.

Some notes about experimental procedure may be mentioned here. Since the ratio of the rates was large, the rate of decomposition was measured by a McLeod gauge and a filter was employed to cut down the intensity of the light during the oxidation experiments. In the direct reaction, comparison was made directly on the oil

TABLE VII. *Photosensitized experiments.*

p_{PH_3}	p_{O_2}	$d[PH_3]/dt$	Ratio of rates	Chain length (ν)	ν for 5 mm PH_3 and 50 mm O_2
		Above the upper limit			
1.98	37.5	0.93×10^{-2} mm/min. in 85 cc I 0.15	19.2	38	53
2.00	—	5.3×10^{-4} mm/min. in 514 cc I 1.00			
8.0	81.0	3×10^{-2} mm/min. in 85 cc I 0.15	10.4	21	34
8.0	—	3.2×10^{-3} mm/min. in 514 cc I 1.00			
6.8	68	8.4×10^{-2} mm/min. in 85 cc I 0.15	8.4	17	43
6.7	—	11×10^{-3} mm/min. in 514 cc I 1.00			
		Below the lower limit			ν for 0.5 mm PH_3 0.5 O_2
0.85	0.36	67×10^{-2} mm/min. in 85 cc I 0.15	480	10	820
0.79	—	0.93×10^{-2} mm/min. in 514 cc I 1.00			
0.83	—	0.93×10^{-2} mm/min. in 514 cc I 1.00	504	10	830
0.83	0.36	2.52×10^{-2} mm/min. in 85 cc I 0.0054			

At the lower limit explosion occurred with 0.83 mm PH_3 and 0.45 mm O_2.

Direct reaction

p_{PH_3}	p_{O_2}	Rate*	Chain length (ν)	ν for 0.5 mm PH_3 and 0.5 mm O_2
		Below the lower limit		
0.254	—	0.075	310	1200
0.254	0.337	11.6		
0.267	—	0.070	400	800
0.254	0.513	14.0		
		Above the upper limit		
8.23	121.4	54.0	72	210
8.64	—	1.5		
8.35	138.1	38.8	47	220
8.40	—	1.65		

* Multiply by 1.27×10^{-2} to give mm/min.

manometer. The rate of decomposition of phosphine was determined by measuring the pressure of hydrogen after the phosphine had been condensed out by liquid air. The ratio of the rates is doubled to give the chain length, for the quantum yield of the dissociation is 0.5.

First of all, it will be seen that, below the lower limit, the chain lengths for the direct and photosensitized experiments are nearly the same. Above the upper limit, however, the chain length (calculated from the relative velocities) in the direct reaction is about five times that obtained in the sensitized oxidation. This confirms the kinetic results about initiation by oxygen and moreover gives the value of A, the number of chains started per excited Hg atom deactivated by oxygen; it is 0.2. The kinetic experiments also yield information about the nature of initiation by oxygen. There is some doubt as to the products of reaction when a $^3P_1$ Hg atom collides with an oxygen molecule. If the low efficiency of initiation were due to the deactivation, by

collision or by radiation, of an excited oxygen molecule of very short life and if initiation be brought about by collision of this excited molecule with phosphine, then it may easily be shown that the initiation factor will assume the form $[PH_3]/[O_2]$ and hence the kinetic equation would become

$$-d[PH_3]/dt = \text{const.}\ [PH_3]^2/[O_2]^3,$$

which does not agree with experiment. Some atom or molecule must emerge from the collision which is not subject to such easy removal as an excited O_2 molecule; the most probable reaction is

$$Hg\ (^3P_1)+O_2 \rightarrow HgO+O,$$

the O atom reacting with the first PH_3 molecule it encounters.

One of the consequences of the theory of branched chains is that the explosion limit curve is a line of equal chain length. Therefore if the chain length be calculated below the lower limit and above the upper limit, and the results extrapolated to these limits employing the appropriate equations, then similar values should be obtained. Such a calculation has been made and the results are given in the last column of Table VII. Although the values of ν are of the same order of magnitude, it must be pointed out that at the upper limit, the chain length is five times shorter than at the lower limit.

The chain length measurements above the upper limit provide the material for a calculation of k_6. From the equation already given, the chain length is represented by

$$\nu = \frac{-d[PH_3]/dt\ (\text{oxidation})}{-d[PH_3]/dt\ (\text{decomp.})} = \frac{k[PH_3]}{k_6[O_2]^2}.$$

Substituting from Table VII, $\nu = 200$, $[PH_3] = 8.4$ and $[O_2] = 138.1$ mm $k/k_6[O_2] = 3300$. Since the propagation collisions are nearly 100 percent efficient, 3300 represents the ratio of the number of bimolecular to trimolecular collisions at 146 mm. Now it is generally assumed that at atmospheric pressure this ratio is 10^3, at 146 mm, it will be $760/146 \times 10^3 = 5200$ and therefore every second ternary collision is effective in destroying X_O. This result may be arrived at in another way. If the kinetics of the stable reaction and of the explosion are exactly similar, then from the above analysis the corresponding equation for the upper limit may easily be deduced by placing the probability of branching $(\alpha-1)$ in the equations for the stationary concentration of the carriers

$$d[X_O]/dt = I + \alpha k[X_P][O_2] - k[X_O][PH_3] - k_6[X_O][O_2]^2 = 0,$$

$$[dX_P]/dt = k[X_O][PH_3] + k[X_P][O_2] = 0,$$

therefore

$$[X_O] = I/\{(1-\alpha)k[PH_3] + k_6[O_2]^2\}. \quad (29)$$

The condition for explosion is that

$$(\alpha-1)k[PH_3] = k_6[O_2]^2, \quad (30)$$

which is exactly in agreement with Dalton's experiments except at high phosphine pressures and also with experiments made during this investigation. To calculate $k/k_6[O_2]$, it is necessary to know $(\alpha-1)$. The chain length is 10^3 at the lower and 2×10^2 at the upper limit, the probability of branching is, respectively, 10^{-3} and 5×10^{-3}. At the upper limit, 5 mm PH_3 and 50 mm O_2, $k/k_6[O_2]$ is 10^4 and 2×10^3. At 55 mm, the ratio of bi- to trimolecular collisions is 1.5×10^4. The agreement is not quite so good with $(\alpha-1)$ obtained from the upper limit results.

A third method, however, obviates the necessity of determining $(\alpha-1)$ and k. At the lower limit

$$(\alpha-1)k[PH_3] = K/[O_2] \quad (31)$$

and at the upper limit

$$(\alpha-1)k[PH_3] = k_6[O_2]^2 \quad (32)$$

or

$$K/[O_2]^3 = k_6, \quad (33)$$

K can be calculated from the dimensions of the reaction tube and mean free path of the chain carriers in the gas. k_6 may then be evaluated and from it the efficiency of the trimolecular collisions. Semenoff[10] has made the calculations using Dalton's results and finds that 0.4 ternary collisions are effective.

Another check on the interrelationships between the stable and explosive reaction can be

[10] Semenoff, Phys. Zeits. d. Sow. **4**, 714 (1934).

made. The whole explosion curve may be represented by the equation

$$(\alpha-1)k[PH_3]=K/[O_2]+k_6[O_2]^2, \quad (34)$$

obtained on adding (31) and (32). For $[PH_3]$ to be a minimum, then by differentiating (34) with respect to $[O_2]$.

$$[O_2]=3(K/2k_6)^{\frac{1}{3}}. \quad (35)$$

From the results shown in Fig. 4, the minimum occurs at 4.6 mm O_2. Similarly, ν below and above the limit is given by

$$\left.\begin{aligned}\nu_{\text{lower}}&=k/K\cdot[PH_3][O_2],\\ \nu_{\text{upper}}&=k[PH_3]/k_6[O_2]^2\end{aligned}\right\} \quad (36)$$

or

$$\nu=k[PH_3]([O_2]/K+1/k_6[O_2]^2).$$

Hence

$$d\nu/d[O_2]=k/K\cdot[PH_3]-2k[PH_3]/k_6[O_2]^3=0$$

or

$$[O_2]=(K/2k_6)^{\frac{1}{3}}$$

is the condition for the chain length to be maximum. Thus the maximum in the chain length curve should occur at the same oxygen pressure as the minimum in the explosion curve. Fig. 4 shows that these anticipations are realized. In the figure of the preliminary notice of this work,[11] the rate of reaction was plotted against the pressure of the oxygen, but it was also pointed out that the curve would have to be suitably corrected for deactivation of the mercury atoms by oxygen. On account of initiation by oxygen, however, the corrections to be made are small, so that the curve does represent the variation of chain length with oxygen pressure. This is more easily seen from Table VIII where the expression, $Z=[PH_3]+0.5A[O_2]/\{[PH_3]+0.5[O_2]+37\}$ is evaluated for different oxygen pressures.

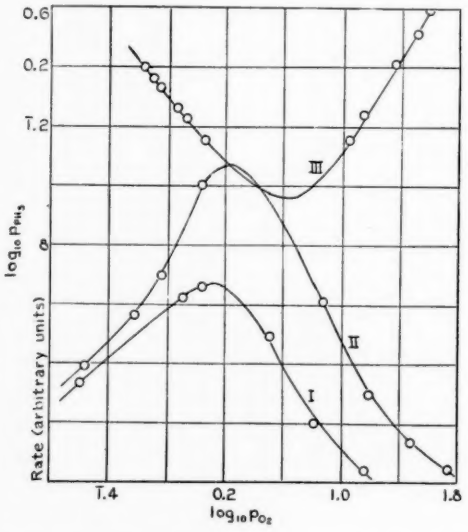

FIG. 4. Curve I, photosensitized reaction $p_{PH_3}=0.130$; II direct reaction $p_{PH_3}=0.260$ mm; III lower and upper limit, thermal explosion.

TABLE VIII. *Variation of initiation factor with oxygen pressure.* $[PH_3]=0.1$ mm

$[O_2]$	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0	50.0
Z	0.20	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20

The photosensitized results are also plotted in Fig. 4. The position of the minimum in the explosion curve, which is 0.212 mm PH_3 and 4.62 O_2, was calculated from Eq. (34).

EFFECT OF RATE OF STARTING OF THE CHAINS ON THE POSITION OF THE LIMITS

Excepting for the moment the oxidation of phosphorus and of phosphine, there is abundant evidence that the position of both limits is dependent on the rate at which chains are started. In the hydrogen-oxygen reaction, for example, it has been established that hydrogen atoms produced photochemically,[12] thermally[13] and electrically,[14] oxygen atoms[14] and chlorine atoms[15] all reduce the ignition temperature. Moreover, even at room temperatures, conditions simulating the lower limit may be obtained with spark ignition.[16] The action of nitrogen peroxide in reducing the temperature of ignition of hydrogen, carbon monoxide, methane, etc., may also be a question of the rate of starting affecting the limits. Similarly, the limits in the oxidation of

[11] Nature **131**, 690 (1933).
[12] Farkas, Haber and Harteck, Zeits. f. Elektrochemie **36**, 711 (1930); Taylor and Salley, J. Am. Chem. Soc. **55**, 96 (1933).
[13] Haber and Oppenheimer, Zeits. f. physik. Chemie **B16**, 443 (1932).
[14] Semenoff, Trans. Faraday Soc. **29**, 606 (1933); Phys. Zeits. d. Sow. **4**, 753 (1934).
[15] Norrish, Proc. Roy. Soc. **A135**, 334 (1931).
[16] Thompson, Trans. Faraday Soc. **28**, 308 (1932).

sulphur,[17] carbon disulphide[18] and hydrogen sulphide are considerably altered by suitable stimuli. Examples may be easily multiplied, but the situation can be summarized by the statement that, in those reactions where the limits are temperature dependent and where explosion occurs at elevated temperatures, the position of both limits is dependent *to some extent* on the rate of initiation. The chain hypothesis alone does not therefore wholly express the condition for explosion, in addition, some temperature dependent factor must be introduced to provide an adequate explanation for the phenomena. With phosphorus and phosphine, it is different, the propagating collisions are almost 100 percent efficient and the efficiency is so high that it cannot be dependent on temperature to any important degree. Similarly, the termination reactions at the walls and in the gas phase do not require activation. In these two examples, then, it is to be expected that the pure chain explosion would occur, and that the condition for explosion would be adequately expressed by the statement that the product of the probabilities of termination and of branching is equal to unity, from which it at once follows that the explosion pressure should be quite independent of the rate of starting. The test is rather a crucial one for some parts of the chain theory. Some time ago, it was applied to the lower limit of phosphine[19] and a very considerable lowering of the limit was obtained. The curious fact was that the effect persisted for a time much longer than the life of the reaction chains. Later it was shown[20] to be due wholly to an alteration of the surface upon which the chains terminated. In the experiments to be described below, the experiment has been repeated at the upper limit which is, of course, unaffected by wall conditions (more strictly the termination reaction only). Initiation was effected by the light from the mercury lamp (water-cooled).

Some indication of the behavior to be expected has already been given, since it has been shown that the chain lengths at the lower and upper limit are not identical. Apparently the explosion can occur more easily at high pressures in that such a long chain is not necessary.

Preliminary experiments showed at once that there was a considerable displacement of the upper limit to higher pressures, provided the tube was illuminated during expansion. Several experiments were carried out in which the gases were illuminated for a considerable time (min.) and allowed to stand for intervals of from 0.5 to 10 min. before expansion, but no displacement could be detected. Table IX contains a number of typical results.

TABLE IX.

Expt. No.	Initial press. p_{PH_3}	Initial press. p_{O_2}	Total press. at explosion	Conditions of illumination
561	6.5	103	72	during expansion
562	6.4	99	26	none
563	6.6	99.5	26	see text
565	5.3	103	57.3	during expansion
566	6.4	112	65	" "
567	4.7	95	56.5	" "

Expt. No.	Initial press. p_{PH_3}	Initial press. p_{O_2}	Total press. at explosion	Intensity
570	7.5	113	63.5	1.00
571	7.5	113	43.5	0.15
572	6.5	100	38.5	0.15
574	7.4	100	56.5	0.15
575	7.3	106	63.5	1.00
577	4.8	111	42.3	1.00
578	8.1	101	80.0	1.00

* Rate of stable reaction at initial pressure 0.13 mm/min., $I = 1.00$.

Experiments 561 to 563 may be particularly mentioned. The initial pressures were all practically the same, but the explosion pressure has been increased by illumination from 26 to 72 mm. In experiment 563 illumination was continued during expansion until the pressure was only 2 mm above the upper limit (72), the light was cut off and the expansion continued, but the pressure had to be reduced to 26 mm to obtain explosion. The time for the pressure to fall 2 mm was not more than 2 sec. so that the lifetime of the effect cannot exceed 2 sec. It is therefore quite different from the lower limit phenomenon which persists for several minutes. The effect of intensity was further investigated in the following way. Instead of plotting upper limit curves for different intensities two mixtures of constant composition were employed. Since expansion does not alter the composition, the displacement of the ex-

[17] Semenoff and Rjabinin, Zeits. f. physik. Chemie **B1**, 192 (1928).
[18] Ritchie and others, Proc. Roy. Soc. **A137**, 511 (1932).
[19] Clusius and Hinshelwood, Proc. Roy. Soc. **A129**, 589 (1930).
[20] Melville, Proc. Roy. Soc. **A138**, 389 (1932).

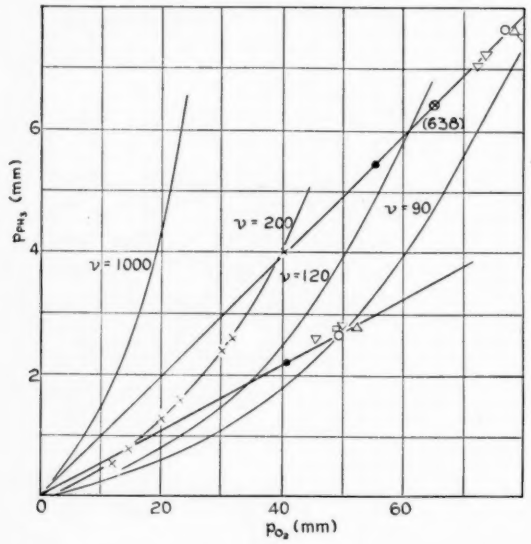

FIG. 5. Displacement of upper limit by illumination. Rate, $\bullet \equiv 5\times10^{-5}$ mm/sec. (2.0×10^{10} quanta per sec.) $\oplus \equiv 10^{-4}$, $\odot \equiv 1.7\times10^{-4}$, $\Delta \equiv 3.3\times10^{-4}$, $\square \equiv 5.4\times10^{-4}$, $\nabla \equiv 37\times10^{-4}$.

plosion limit along the expansion line can be regarded as a measure of the effect. The data are plotted in Fig. 5.

The intensity could not be increased to higher values since the velocity of the reaction was then sufficient to remove considerable amounts of phosphine and oxygen.

These results then prompt a further question as to whether, at the lower limit, in addition to the ordinary displacement owing to the change in surface, there is a transient effect similar to that at high pressures. The procedure adopted was to use a constant pressure of phosphine and allow oxygen to leak in through the needle valve and record the explosion pressure on the oil manometer. The intensity of the light was 0.15 on the same scale as that given in Table X. The results listed in Table X show the conditions of illumination and are recorded in the order in which the experiments were carried out.

Comparing Nos. 625, 626 and 633 with the remainder, it will be seen that the explosion pressures, in which there has been illumination, are somewhat lower than those in its absence, thus confirming previous results. It does not appear to matter whether the light is switched off sometime before the explosion or whether it is left on right up to the explosion limit. It will also

TABLE X. *Lower limit, silica surface.*

No.	p_{PH_3}	p_{O_2} at explosion	$p_{PH_3}+p_{O_2}$	Conditions of illumination
622	0.74	0.61	1.35	continuous
623	0.81	0.54	1.35	until $p_{PH_3+O_2}$ 1.26
624	0.80	0.49	1.29	" " 1.26
625	0.80	0.79	1.59	none
626	0.77	0.76	1.53	none
627	0.80	0.49	1.29	until $p_{PH_3+O_2}$ 1.26
628	0.78	0.48	1.26	continuous
629	0.76	0.44	1.20	until $p_{PH_3+O_2}$ 1.18
630	0.76	0.64	1.40	" " 1.12
631	0.76	0.48	1.24	" " 1.18
632	0.76	0.64	1.40	" " 1.12
633	0.77	0.74	1.51	none

be observed that if illumination be stopped at a low pressure of oxygen (expts. 630 and 632) the explosion limit is a little higher than that where illumination has been continued up to higher oxygen pressures. The conclusion then is that the transient effect, obtained at the upper limit, is not in evidence at the lower limit.

To demonstrate more clearly the sensitiveness of the upper limit to the stationary concentration of X_O, the following experiment (638) and calculations were made. A mixture of 12.0 mm, phosphine and 114 mm oxygen was prepared, illuminated during expansion when explosion occurred at 71 mm. Thus the intensity of the light was a somewhat greater (0.30) than 0.15 in the experiments in Table X, as is seen if the explosion point is placed on the upper expansion line of Fig. 5. A second mixture was then prepared and pumped down to 75 mm. At this pressure, the rate of oxidation of phosphine was 9.3×10^{-5} mm/sec. in a volume of 85 cc: the calculated chain length is 110. The number of quanta entering the reaction tube is thus 4×10^{10} sec^{-1}. At 75 mm, a molecule experiences about 10^6 ternary collisions per sec., or the interval between such collisions is 10^{-6} sec., which is therefore the mean life of X_O. The rate of production of X_O may be taken as the rate of dissociation of phosphine or $9.3\times10^{-5}/110$ mm/sec. $\doteqdot 10^{-6}$ mm/sec. and the stationary concentration is thus 10^{-12} mm. According to Table X, when the stationary concentration of X_O attains 10^{-11} mm, the limit ceases to be affected. When such a small concentration of

carriers displaces the limit so much, it is not at all surprising that traces of water vapor and possibly other gases and also changes of temperature[9] exert a comparatively large influence. This, in turn, suggests that the displaced limit is really the true explosion limit and that the one observed in the thermal reaction is particularly low because of the fact that a sufficient number of chains do not start to fulfill the conditions required by the chain theory. It this were the case, the chain length at the displaced limit would be 10^3, whereas it is only 10^2. Both the probability of branching and of termination are processes involving the reaction of only one carrier and thus should be unaffected by variations in the concentration of that carrier.

The following theory may be advanced to account for these observations. As a result of a slow thermal reaction above the upper limit ozone is formed. Likewise in the stable photoreaction ozone is produced in much larger amounts as a consequence of the termination of the chains. Ozone increases the explosion pressure for every collision between X_P and O_3 gives rise to two X_O's, i.e., the probability of branching is increased. Ozone is destroyed by reaction with phosphine, but this is a comparatively inefficient reaction. In the photoreaction ozone is also decomposed photochemically. No chains are started, however, by these two processes. Expressing all these assumptions in the usual manner, the following equations are obtained

$$\left.\begin{aligned} d[O_3]/dt &= k_6[X_O][O_2]^2 - k[X_P][O_3] \\ &\quad - k_{10}I_0[O_3] - k_{11}[PH_3][O_3] = 0, \\ d[X_O]/dt &= I_T + I_P + \alpha k[X_P][O_2] \\ &\quad + 2k[X_P][O_3] - k[X_O][PH_3] \\ &\quad - k_6[X_O][O_2]^2 = 0, \\ d[X_P]/dt &= k[X_O][PH_3] - k[X_P][O_2] \\ &\quad - k[X_P][O_3] = 0, \end{aligned}\right\} \quad (37)$$

where I_O is proportional to the intensity of the light decomposing the ozone, I_T and I_P are the thermal and photo rates at which chains are started. Solving and simplifying these equations, the condition for explosion is that

$$(\alpha-1)k[PH_3] + 2k[O_3]/[O_2] = k_6[O_2]^2, \quad (38)$$

from which it is evident that ozone facilitates explosion. The quantity required to exert a large effect is small. From Fig. 5, with 2 mm PH_3, the pressure of O_2 at the limit should theoretically be 12 mm; experimentally it is 26 mm and therefore if $(\alpha-1)=10^{-3}$ solution of (38) gives $[O_3]=10^{-2}$ mm. On solving (37) for $[O_3]$ above the explosion limit

$$[O_3] = (I_T + I_P)/(I_T + I_P + k_{11}[PH_3]),$$

which shows at once that in the photo-experiments when $I_P \gg I_T$ and $k_{11}[PH_3]$, this expression is independent of intensity in agreement with observation. Moreover the displacement at high oxygen pressures should not be quite so much as at low pressures. Examination of Fig. 5 reveals that the explosion points on the upper expansion line lie somewhat to the left of the curve for $\nu=90$. At low values of I_P, $k_{11}[PH_3]$ comparable with I_P, the displacement of the limit will be proportional to the intensity. In order to preserve the form of the explosion curve for the dark reaction it is necessary to assume that $I_T \sim [PH_3][O_2]$ in which case the term containing $[O_3]$ becomes independent of phosphine and oxygen pressure.

On account of the sensitiveness of the upper limit to the stationary concentration of chain carriers, an attempt was made to measure the rate of the thermal reaction outside the explosion limits. For this purpose a quantum counter sensitive to radiation of $\lambda < 2800$A and capable of detecting 50 quanta per minute was employed.[21] Two mixtures were made up (a) below the lower limit, 0.396 mm PH_3 and 0.37 mm O_2, $\nu=250$, (b) above the upper limit 8.7 mm PH_3, 132 mm O_2, $\nu=50$, and the tubes placed in close proximity to the counter, but no radiation could be detected. It may of course be that there is reaction accompanied by radiation which does not affect the counter.

Elsewhere it has been suggested that oxidations brought by nitrous oxide instead of by oxygen cannot proceed explosively by branching chains, although straight chains are readily obtained. Experiments were therefore made with phosphine-nitrous oxide mixtures to see if chains could be started by the photodissociation of the phosphine, but no chain propagation occurred.

In view of these experiments and calculations,

[21] Ouellet, Trans. Faraday Soc. **29**, 486 (1933).

there are consequently good grounds, though the evidence is not direct, for supposing that X_O is an oxygen atom. Furthermore, it is possible that the collision which gives rise to branching is that between X_P and O_2, yielding two oxygen atoms.

The existence of an upper limit can be attributed to two causes (*a*) removal of the chain carriers by a reaction of higher order than that of branching, e.g., phosphine, (*b*) a deactivating influence of the reactants on a collision complex which would otherwise give rise to two chains, e.g. hydrogen, (*c*) other causes not at present included in the theory. It will be a matter for further experiment to decide, by closely examining the relationship between the kinetics of the stable and explosive reactions, which mode of deactivation causes the upper limit in other chain reactions. Such experiments may reveal whether, as in the case of phosphine, explosion occurs at the upper limit more readily than theory predicts.

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The Disappearance of Hydrogen in the Presence of Potassium and Lithium Ion Sources

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The disappearance of hydrogen in the presence of iron-alkali catalysts, sources of K^+ ions and a synthetic spodumene mixture, a source of Li^+ ions, was investigated. In these experiments, like those previously reported by the authors, no gas phase reaction was detected which could be attributed to the bombardment of hydrogen by positive ions with speeds up to 565 volts. It was concluded that all cleanup effects could be accounted for by reactions on or within the materials used as ion sources.

FURTHER results on the cleanup of hydrogen in the presence of materials and mixtures used as ion sources clear up a number of points upon which apparent disagreement in results was reported and conflicting opinions expressed.[1, 2]

In the previous paper by the authors it was found that with the platinum-coated glass anode source of positive ions,[3] an effect was observed, which was found to be due, not to the positive ions but to a surface reaction intimately associated with the electrolysis of potassium through the glass anode.

The present paper deals with further results from similar tests with an iron alkali catalyst, a source of potassium ions, and with an artificial spodumene, a source of lithium ions.

The apparatus, Fig. 1, was essentially the same as in previous work,[2] except that in some of the experiments a grid was used to accelerate the ions to their full velocity as soon after leaving the filament as possible. Pressures were measured with a Pirani gauge.

The results from an Fe-K catalyst (No. 920, containing 0.2 percent K_2O) source are shown in Fig. 2. These results were obtained after the catalyst had been reduced at about 650°C for a total time of 24 hours. No definite cleanup due to the positive ions was observed. On the

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[1] Leipunsky and Schechter, Zeits. f. Physik **59**, 857 (1930). A. Schechter, Zeits. f. Physik **75**, 671 (1932). A. C. G. Mitchell, J. Frank. Inst. **210**, 269 (1930). Zeits. f. Physik **78**, 138 (1932).

[2] C. H. Kunsman and R. A. Nelson, Phys. Rev. **40**, 936 (1932).

[3] F. G. Cottrell, C. H. Kunsman and R. A. Nelson, Rev. Sci. Inst. **1**, 654 (1930).

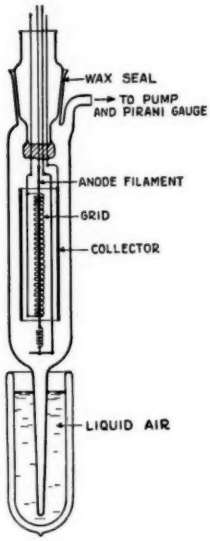

FIG. 1. Experimental tube.

contrary a marked slowing up of the cleanup rate occurred at about the time the potential was turned on. The added cleanup to be expected, at the rate of one molecule per ion, is shown by the broken line. From this it is apparent that the changes in the primary cleanup rate itself would entirely mask any added phenomena of this order of magnitude due to the positive ions. The positive ion current is plotted in the same figure, the average value being about 5×10^{-7} amp.

Typical results from reduced Fe-Al-K catalyst (No. 922 containing 1 percent Al_2O_3 and 0.26 percent K_2O) are given in Figs. 3 and 4. Curve (1), Fig. 3, in effect is a continuous curve up to 83 minutes when a break is observed which is definitely associated with the striking and continuation of a glow discharge. The superimposed straight lines, as in the previous curve, are drawn for the purpose of analysis and discussion only. In the case of the glow discharge, when the current increased from 6×10^{-6} to 9×10^{-5} amp., the cleanup rate increased by an amount corresponding to about 0.3 of a molecule per ion. It was found in separate tests with this tube that at these hydrogen pressures a glow discharge could occur and be maintained at potentials as low as 200 to 250 volts, while in other tubes and under different conditions higher potentials were required. Curve (2) was taken with a tube containing a grid and again there was no evidence of a cleanup due to positive ions; any changes occurring in the slope of the curve were independent of the positive ion currents. Before this test was made the catalyst had been reduced for a period of about 70 hours at temperatures of about 650–700°C.

Fig. 4 gives the results of two tests on catalyst No. 922. The tube contained no grid but a plate potential of 300 volts was used to speed up the K^+ ions in the presence of hydrogen.

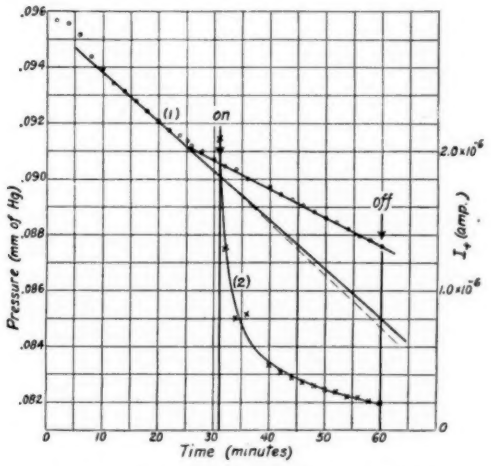

FIG. 2. K^+ ions and hydrogen in tube without grid. Fe-K oxide catalyst No. 920 as ion source. Temperature about 750°C. Curve (1), hydrogen pressure; curve (2), positive ion current with a plate potential $V_p=-310$ volts. Broken line indicates calculated decrease at one molecule per ion.

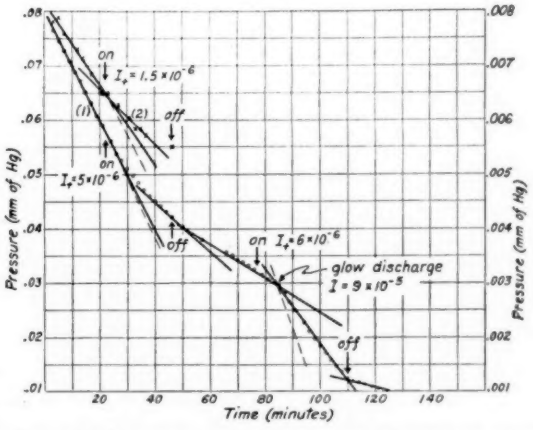

FIG. 3. K^+ ions and hydrogen. Fe-Al-K oxide catalyst No. 922 as ion source. Plate potential $V_p=-310$ volts. Temperature about 750°C. Curve (1), ordinates at left—tube without grid; curve (2), ordinates at right—tube with grid. Broken line indicates calculated decrease at one molecule per ion.

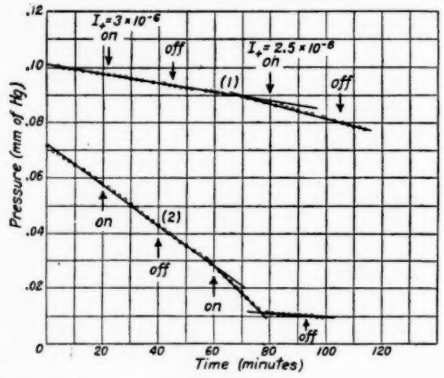

FIG. 4. K^+ ions and hydrogen in tube without grid. Fe-Al-K oxide catalyst No. 922 as ion source. Plate potential $V_p = -300$ volts. Temperature about 750°C.

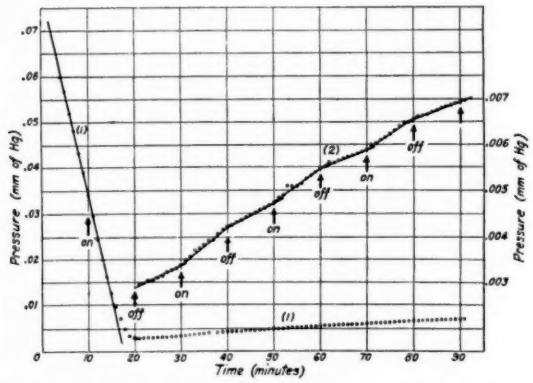

FIG. 5. Li^+ ions and hydrogen in tube with grid. Synthetic spodumene as ion source. Grid potential $V_g = -183$ volts, $V_p = -(183+26)$ volts; temperature about 800 to 850°C. Curve (1), ordinates at left; curve (2), ordinates at right.

After curve (1) was obtained a small amount of hydrogen was pumped from the tube, the test continued and curve (2) obtained. No change in rate or breaks in the curve can be associated with the 300 volts potential or speed of the positive ions. In curve (1), at 80 minutes or when the potential was turned on, an increase in rate was observed which started about 10 minutes before this time. Other tests were made using potentials up to 565 volts with results similar to those observed at the lower potentials.

Investigations of the reduction of the catalyst coated filament have shown several things. First, complete reduction is not necessary for good ion emission, in fact the emission seemed to reach a maximum when the catalyst was from 5 to 10 percent reduced. Secondly, in order to make the reduction process as complete as possible it should be carried out in either a flow system, or with an absorption bulb at reduced temperature, that is, under conditions which remove the products of the reduction as rapidly as they are formed. Thirdly, the catalyst material was ineffective as an ion source by the time the material was completely reduced. There is thus considerable weight of evidence in favor of concluding that in the case of the iron catalyst, the residual cleanup observed without ions is due to reduction of the catalyst by hydrogen and not thermal dissociation of the hydrogen as assumed by Leipunsky and Schechter.

The results from a spodumene source of Li^+ ions are given in Fig. 5. The hydrogen cleanup was extremely rapid at the start and no effect could be observed due to the accelerated positive ions. After 20 minutes, there was an increase in pressure, as shown in curve (1). This was of considerable interest and gave further information on the cleanup reaction. Curve (2) shows this part of the curve plotted to a scale of ordinates magnified by a factor of ten. The accelerating potential was turned on and off at the times shown on curve (2). The grid and plate were -183 and -209 volts, respectively, with reference to the filament. The effect of applying the accelerating potential is quite evident. Apparently this curve consists of a cleanup of the hydrogen in the tube, accompanied by a slow gassing which can only be detected after the hydrogen has disappeared. The rate of gassing appears to be markedly increased by the application of an accelerating potential for the positive ions.

This interpretation was confirmed by further tests on gassing alone. Typical results are shown in Fig. 6. For these tests the tube was pumped to a good vacuum (less than 10^{-6} mm Hg), trapped off, and the filament glowed as for a hydrogen run. The pressure change was then observed as the accelerating potential was turned on and off at ten minute intervals. Curve (1) shows the results obtained when a run was made without liquid air on the condensation trap. This curve displayed the same characteristics as Fig. 5, showing an increased rate of gassing when the potential was on. Curve (2) was taken with liquid air on the trap, and is similar to (1), but

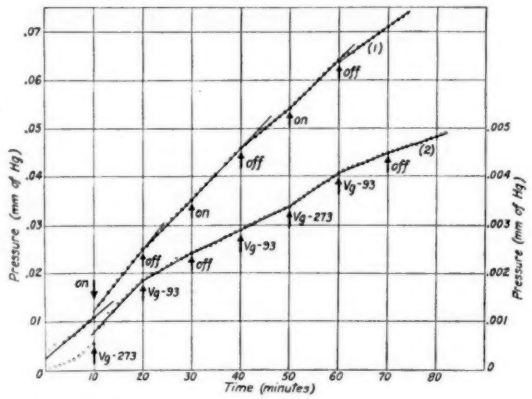

FIG. 6. Li^+ ions in evacuated tube with grid. Synthetic spodumene as ion source. Curve (1), gassing at room temperature (no liquid air on trap); ordinates at left; $V_g = -93$ volts, $V_p = -(93+13)$ volts. Curve (2), gassing with liquid air on trap; ordinates at right; $V_p = V_g - 18$ volts. Temperature 800 to 850°C.

in addition shows a variation in rate which was a function of the potential. As in the case of the catalyst source, tests up to 565 volts gave no additional information on the hydrogen cleanup.

As seen from these two curves there was about 15 times the gas present at room temperature as at liquid air temperature. From a number of similar comparison tests one may conclude that from 5 to 10 percent of the gas given off was noncondensable in liquid air, and was probably nitrogen and oxygen. A rough analysis of the condensable gases was made as follows. After pumping off the noncondensable gases, the liquid air bath was replaced by a mixture of carbon dioxide snow (dry ice) and acetone. After some time the gases evolved from the trap at −78°C were collected with a Toepler pump. The collected gas was then tested for CO_2 by absorption in an alkali solution. This test showed that about 90 percent of this gas was CO_2.

The remainder of the gas which was still condensed at −78°C was water vapor as shown by its behavior in the McLeod gauge, vapor pressure, and condensation.[4] The average gaseous products from the spodumene materials used in these experiments were therefore about 5 to 10 percent N_2 and O_2, 15 to 22 percent CO_2 and 63 to 80 percent water vapor.

The interpretation of these results is similar to that given in the previous paper.[2] In the case of the catalyst filaments a continuous slow reduction of the catalyst material accounts for the observed cleanup. The spodumene is more complicated since as herein shown it breaks down spontaneously when heated, this decomposition being further hastened by applying a potential which draws out positive ions. The spodumene[5] was an artificial product made up by fusing a mixture of Li_2CO_3, $Al(NO_3)_3$ and SiO_2, so that there was probably at least all of the following compounds present; Li_2SiO_3, Li_2CO_3 and $LiNO_3$. These compounds probably break up as follows: $2Li_2SiO_3 \rightarrow 4Li + 2SiO_2 + O_2$; $2Li_2CO_3 \rightarrow 4Li + 2CO_2 + O_2$; $2LiNO_3 \rightarrow 2Li + 2NO_2 + O_2$.

Thus if the filament is run in a vacuum, CO_2, O_2, N_2 or oxides of nitrogen will be evolved and drawing positive ion current should accelerate the gassing as was found experimentally. When hydrogen is present its cleanup is accounted for by combination with the oxygen evolved.

CONCLUSIONS

The additional information obtained from these tests gave no indications whatever of a gas phase reaction due to the bombardment of hydrogen by positive ions with speeds up to 565 volts. All effects may be accounted for by the reactions on or within the material used as ion sources. These effects are accelerated by electrolysis. The additional cleanup of hydrogen due to K^+ and Li^+ ions in the gas phase if it exists at all is certainly less than 0.1 molecule per ion at speeds of from 250 to 565 volts. The gaseous product from the synthetic spodumene material used as ion sources consisted of about 5 to 10 percent N_2 and O_2, 15 to 22 percent CO_2 and 63 to 80 percent water vapor.

The writers wish to thank Dr. R. T. Milner of this laboratory for suggestions in collecting the gases and also for their chemical analysis.

[4] N. R. Campbell, Proc. Phys. Soc. (London) **33**, 287 (1921).

[5] E. J. Jones, Phys. Rev. **44**, 707 (1933).

The Photoisomerization of the o-Nitrobenzaldehydes

I. Photochemical Results

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Numerous disparate explanations have been advanced for the observed quantum yield in the photoisomerization of o-nitrobenzaldehyde. The authors decided to gather further data on this reaction, varying such factors as the weight of the molecule and the physical state of the material. The results indicate that the reaction occurs intramolecularly, but that for o-nitrobenzaldehyde itself the quantum efficiency is nearly one-half in all cases. A detailed consideration of the mechanism is deferred to the second portion of this paper.

INTRODUCTION

THE reaction of o-nitrobenzaldehyde to give o-nitrobenzoic acid upon illumination has been found to proceed entirely by an intramolecular rearrangement[1] with no side or reverse reaction, and the same may be said of the analogous reactions of 2,4-dinitrobenzaldehyde and 2,4,6-trinitrobenzaldehyde.[2]

The apparent simplicity of the reaction is belied by the quantum efficiency, which for the mono-nitro compound is almost exactly one-half.[3] This surprisingly low quantum efficiency, together with its nearness to a simple fraction, have been the subject of a considerable body of experimental work and theoretical discussion.[3, 4, 5, 6] Conflicting explanations have been advanced, all but two of which have been either abandoned by their authors or disposed by the work of Zimmer.[5] The remaining ones are his and that of Wegscheider,[6] who postulates simply that of the absorbed quanta, half are lost by deactivation and the remainder cause reaction.

Zimmer's hypothesis is that every absorbed quantum splits off an oxygen atom; whereupon half of such atoms return to the nitroso group and the other half react with the neighboring aldehyde. Some objections to this view may be given. First, one might expect some evolution of oxygen molecules, if not from o-nitrobenzaldehyde, at least from nitrobenzene. Second, m- and p-nitrobenzaldehyde should also show photoisomerization, which they do not. Third, the dissociation of a nitro bond by light of wavelength longer than 1900A is energetically improbable, but the reaction occurs at least to 4360A. Fourth, Zimmer's work was with a mixture of the aldehyde and pyrogallol, in which an entirely different reaction might occur.

A quantum yield of one-half in the reaction of benzoquinone with ethyl alcohol[7] was shown to be varied widely upon replacing the hydrogens of the benzene ring with other substituents or upon changing the nature of the solvent,[8] from which the conclusions were drawn that the low quantum yield was due to a collisional deactivation of part of the quinone molecules which had absorbed light, and that the value of one-half for benzoquinone in pure alcohol was fortuitous.

The possibility of a similar set of circumstances in the nitrobenzaldehyde reaction led the authors to re-investigate the latter, under conditions which might be expected to produce a change in quantum yield. Thus, the number of nitro groups in the molecule was changed, and the reaction in acetone solution was compared with that in a nonpolar solvent and in the solid phase.

APPARATUS, MATERIALS AND METHODS

The arc, prism monochromator, and thermopile used have been described.[7] As in the investigation of Weigert and Brodmann,[3] the conduc-

[1] Ciamician and Silber, Ber. **34**, 2040 (1901).
[2] Fiedländer and Cohn, Ber. **35**, 1267 (1902); Sachs and Kempf, Ber. **35**, 2707 (1902).
[3] Weigert and Kummerer, Ber. **46**, 1207 (1913); Weigert and Brodmann, Zeits. f. physik. Chemie **120**, 24 (1926); Weigert and Prückner, Zeits. f. physik. Chemie, Bodenstein Festband, 775 (1931).
[4] Bowen, Hartley, Scott and Watts, J. Chem. Soc. **125**, 1218 (1924).
[5] Zimmer, Zeits. f. physik. Chemie **B23**, 239 (1933).
[6] Wegscheider, Monats. f. Chemie **62**, 101 (1933).
[7] Leighton and Forbes, J. A. C. S. **51**, 3549 (1929).
[8] Leighton and Dresia, J. A. C. S. **52**, 3556 (1930).

tivity of the acid formed in the reaction was used for analysis of the product. The bridge and thermostat possessed no novel features. A dipping electrode in a Pyrex test-tube made the cell.

The manipulations of the solutions were orthodox: solutions were exposed in a fused silica cell behind the exit slit of the monochromator. Those in acetone were then diluted with three volumes of conductivity water for analysis. Solutions in ligroin were evaporated and then extracted with a known volume of acetone after exposure, and the solution diluted with conductivity water as before. The conductivity of a blank or unexposed solution was always subtracted, as in the calibration.

Solids were prepared for exposure by fusing a known quantity to a quartz plate and illuminating through the latter, thus reducing scattering; because the crystal interfaces were then perpendicular or parallel to the beam. Enough sample was used to absorb the beam completely. The plate bearing the exposed sample was placed in a beaker, and the aldehyde dissolved with six cc of acetone. Eighteen cc of conductivity water were added and the whole mixed together. Enough of the mixture to cover the glass shell of the dipping electrode was then poured into the conductivity cell. This was always allowed to stand fifteen minutes in the thermostat at 25°C before the conductivity was read. The room temperature was kept between 22°C and 24°C for all but a few measurements.

Acid formed during the reaction did not precipitate from an acetone solution, but did from one in ligroin. In consequence, the liquid became turbid. Reactions in ligroin were accordingly carried out in a broad flat cell which was slid along behind the monochromator slit every few minutes, so that no acid would cling to the front window. In addition, the solution was stirred. After exposure, the ligroin was evaporated and the solid taken up in the usual mixture of acetone and water.

The transmission before and after exposure was measured for those acetone solutions which were sufficiently dilute to transmit appreciably, but the turbidity of the ligroin solutions prevented accurate observations after exposure. For example, a straightforward calculation for 0.04 precent o-nitrobenzaldehyde in ligroin at 3660A gave $\Phi = 0.57$. If, instead, one calculates what the transmission should have been had there been no scattering and uses this value to compute Φ, the result is 0.52.

The measurements and calculations of quantum efficiencies for the reactions in solution were carried out in the manner reported for the quinone-alcohol reaction,[7] with such differences as were made necessary by the difference in materials. The calculation of quantum yields in solids presents two difficulties not usually encountered in solutions. The reaction product piles up at or near the surface exposed to light, making a non-uniform filter, and the reflection from the crystal surfaces is difficult to calculate.

Both effects can be circumvented experimentally. The light scattered from crystal interfaces may be collected in large fractions by a lens of wide aperture and short focus and measured with a thermopile, while to avoid absorption by the reaction product one may extrapolate to the start of the reaction.

It remains to discover the proper method of extrapolation. Consider a crystal divided into infinitesimal layers parallel to its front surface. In the first instant of illumination, a certain fraction of the material in the first layer will be changed, and in the next instant, the same fraction of the remainder, and so on. This process leads to a logarithmic decrement of the reaction rate. In the second layer, the same thing happens, but there is the additional complication that the extinction coefficient of the product differs from that of the original material, and accordingly, the intensity, constant on the first layer, will be exponentially changing on the second. The product of these two exponential factors is itself exponential, so that the reaction rate undergoes a logarithmic decrement in the second layer as well. The argument for the third layer is the same. Indeed, we may expect a similar conclusion for the whole crystal.

Now if the logarithm of the instantaneous value of the quantum efficiency, Φ_i, is plotted against the number of quanta absorbed, N_q, the result should be a straight line. The apparent quantum efficiency, Φ_a, calculated on the basis of the total number of quanta absorbed, is what is measured. A plot of this should also give a straight line, with half the slope of the preceding

one. For, using the slope-intercept formula for the equation of the graph of Φ_i against N_q,

$$\log \Phi_i = mN_q + \log \Phi,$$

where Φ is the true value, obtaining at the start of the reaction, and m is the slope. From the relation for the apparent value,

$$\log \Phi_a = (\log \Phi_i + \log \Phi)/2,$$

we have $\log \Phi_a = mN_q/2 + \log \Phi$. One must, then, plot a number of observed values of $\log \Phi_a$ against N_q and fit a straight line to the points.

In this derivation it has been assumed that the extinction coefficients of reactant and product remain constant. As a matter of fact, particularly in ionic crystals, they will change as the reaction progresses, because of the distortion of the crystal lattice. Some such effect is noticeable in the researches of the Göttingen investigators[9] on the photoreduction of alkali ions in alkali halide crystals. When their results are plotted according to the system here outlined, they yield initial quantum efficiencies close to unity for this process, but the points corresponding to long exposures fall off the line. The high opacity of the alkali halides in the Schumann region may be partly responsible, for the thickness in which most of the reaction occurs is small, and only a short exposure is required to produce almost complete change of the first layers.

The o-nitrobenzaldehyde used was a Kahlbaum product, and was further purified by taking up in benzene to reject the acid which it contained. The solvent was then evaporated and the aldehyde recrystallized four times from dilute alcohol and from hot water. Some of the material was vacuum sublimed, all operations being performed in the dark. The highest melting point reached was 43.5°C. Other reported melting points range from 39.4°C to 46°C.

The 2,4-dinitrobenzaldehyde was synthesized after the method devised by Sachs and Kempf, with the improvements suggested by Lowy and Wescott.[10] After recrystallization from ligroin and from hot dilute alcohol, it melted at 71°C.

The 2,4,6-trinitrobenzaldehyde was obtained from the Eastman Kodak Co. and recrystallized as above. It melted at 119°C.

[9] E.g., Smakula, Zeits. f. Physik **63**, 762 (1930).
[10] Lowy and Wescott, J. A. C. S. **42**, 852 (1920).

The various nitrosobenzoic acids for calibration of the conductivity-concentration curves were prepared by making successive dilutions of the corresponding aldehydes in acetone and insulating till the conductivity of the most concentrated solution showed no further change. These solutions were then each diluted with three volumes of conductivity water and their conductivities read. From each result there was subtracted the conductivity of a corresponding unexposed solution, and the results were plotted.

Experimental Results

The results for a number of determinations in solution are given in Table I, which includes also some molecular extinction coefficients (α). The Roman numerals refer to the three aldehydes.

Table I.

Material	λ	Concentration	Solvent	Φ	α
I	4040	0.03%	acetone	0.46	35.6
	3660	0.5	"	0.51	184
	3660	0.04	ligroin	0.52	181
II	3660	0.5	acetone	0.49	
	"	0.5	"	0.49	
	"	0.1	"	0.48	
	"	0.01	"	0.48	188
III	3660	0.5	acetone	0.65	
	"	0.5	"	0.65	
	"	0.5	"	0.68	
	"	0.1	"	0.69	192
	"	0.1	"	0.63	
	"	0.1	"	0.66	
	"	0.04	ligroin	0.17	1030

Most of the solutions were stirred mechanically during the exposure. For two, nitrogen was used as an atmosphere. The observation of Weigert that oxygen, stirring, and concentration differences do not affect Φ for o-nitrobenzaldehyde was found to hold for the other two compounds also. The change of α and Φ with change of solvent in the last measurement is a field for further investigation.

The results for the reaction in the solids are graphed in Figs. 1 to 3. The points in the first diagram of Fig. 1 were taken before the procedure was well standardized, and the line was fitted to them by minimizing the sum of the squares of the normal deviations. The points for

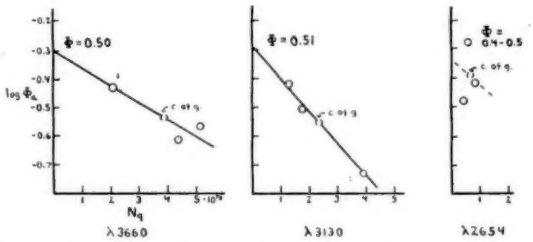

FIG. 1. Apparent and actual quantum efficiencies for the photoisomerization of solid o-nitrobenzaldehyde.

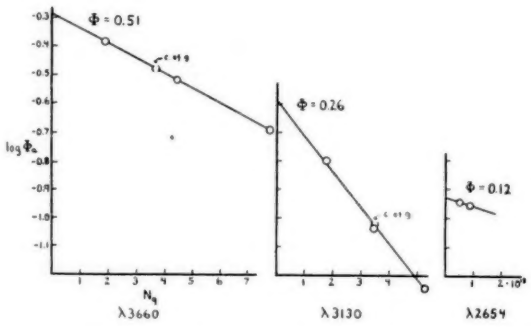

FIG. 2. Apparent and actual quantum efficiencies for the photoisomerization of solid 2,4-dinitrobenzaldehyde.

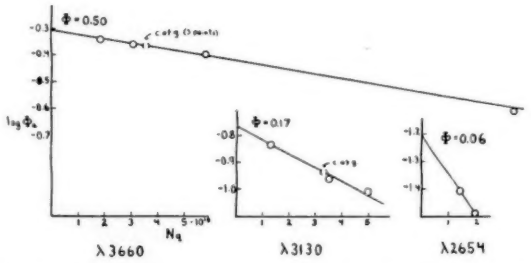

FIG. 3. Apparent and actual quantum efficiencies for the photoisomerization of 2,4,6-trinitrobenzaldehyde.

the mono-substituted compound at 2654A scatter rather badly, but a quantum yield of somewhat less than 0.5 is indicated. The other lines were fitted by inspection; the points are so nearly collinear that analytical devices were unnecessary.

DISCUSSION

Insofar as this work repeats that of Weigert on o-nitrobenzaldehyde in acetone solutions, the two are in agreement. It is true that he found that Φ increased with dilution at 4040A, but he considered this a spurious effect caused by his assumption that α, measured for a concentration of 1 percent, remains constant. Measurement shows that α actually does increase with dilution by the right amount to reduce Weigert's measured Φ's to about 0.5. Bowen, Hartley, Scott and Watts,[4] without the refinements in technique used here, obtained an unweighted average of $\Phi = 0.46$ for solid o-nitrobenzaldehyde, in agreement with the value of 0.5 reported in the present paper. The quantum efficiency for this compound is thus seen to be nearly one-half, in acetone and ligroin solutions, and in the solid state, and over a wave-length range from 4360A to 3130A at least.

It is evident that a simple collisional deactivation hypothesis, such as was applied to the quinone-alcohol reaction, will not suffice to explain these results. The yield determining process must be intramolecular, in accord with the apparent intramolecular nature of the reaction.

The same quantum yield is found for the di-substituted compound, both in solid and solution, at 3660A, where the ortho nitro group does the absorbing, and the same conclusions hold. The case of the tri-substituted compound differs because of the effects of a nitro group on both sides of the aldehyde. Discussion of its behavior must await a quantitative discussion of the intramolecular interactions (part II).

The lower quantum efficiencies found at shorter wave-lengths in the solid state may in every case be plausibly assigned to an inner light filter effect of other portions of the molecule, although this is not the only possibility (part II).

The Photoisomerization of the o-Nitrobenzaldehydes

II. Mathematical Treatment

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The probable course of the reaction, from the absorption of light to the formation of the isomer, is followed in roughly quantitative detail. In this manner, the low quantum yields, surprising at first sight for intramolecular processes, are explained by a consideration of the physical properties of the molecules.

IN the preceding paper it was stated that the process which determines the observed quantum efficiency of one-half in the isomerization of o-nitrobenzaldehyde to o-nitrobenzoic acid must be intramolecular. A consideration of the possible nature of such a process will involve an examination into, first, the bond or group which absorbs the actinic light, second, the relative orientation of the reacting groups, and third, the relative probabilities of energy transfer by resonance between bonds, of deactivation, and of reaction.

A comparison of the absorption spectra of o- and m-nitrobenzaldehyde, nitrobenzene and benzaldehyde[1] shows clearly that for wavelengths longer than about 3100A, the nitro group is the only portion of the molecule which appreciably absorbs. This absorption is presumably effected by the electrons of the two nitrogen-oxygen bonds, the absorption probability in the two being equal.

THE ORIENTATION OF THE NITRO AND ALDEHYDE GROUPS

The relative orientation which may be assumed for the nitro and aldehyde groups involves the question as to whether these groups are freely rotating, or are constrained to a particular position by intramolecular forces. The constraints which need to be treated are those varying with the rotation of the substituents, aldehyde and nitro, which together with the phenylene residue will be chosen as constituents of the molecule. The position-sensitive interactions of these groups, since they bear no free valences, will be made up of second and higher order terms.

It will be recognized that, if one plots the energy of a given configuration as altitude on a contour map, using the rotation of the nitro group as abcissa and that of the aldehyde as ordinate; then the lowest point is the position of stable equilibrium and the height of the lowest pass is the energy required to produce rotation. The first-order interaction between the nitro and aldehyde will be a slight steric hindrance because they are somewhat closer than the sum of their kinetic theory radii. If the groups are supposed to be surrounded by spheres of influence, there will be no change in the magnitude of repulsion on rotation, but this is probably too crude a picture; prolate spheroids doubtless better represent the facts. However, since the shape of these is unknown, the first order repulsion will not be further considered.

The second-order interactions, if calculated according to the theory of London,[2] would also give no constraint to free rotation. However, this theory assumes that the groups possess isotropic polarizabilities, i.e., that an impressed electric field induces the same electric moment for any relative orientation of group and field. This is far from being true in the present case. No measurements of the actual components of the polarizability tensors are possible for the groups under consideration, but such measurements have been made for molecules closely analogous to the groups considered here.[3] Benzene, sulphur dioxide and hydrogen cyanide, that is, are similar to phenylene, nitro and aldehyde. To change the molecular values to fit a corresponding radical, one has to multiply each component for the mole-

[1] Purvis and McCleland, J. Chem. Soc. **103**, 1088 (1913).

[2] London, Zeits. f. Physik **63**, 245 (1930).

[3] Wolf, Briegleb and Stuart, Zeits. f. physik. Chemie **B6**, 195 (1930).

cule by the ratio of the mean polarizabilities of radical and molecule. The radical components, which we shall call α_{11}, α_{22} and α_{33} in descending order of magnitude, are obtained for the principal axes of the group. They are transformed to a coordinate system (x, y, z) embedded in the molecule by the customary formula. For example:

$$\alpha_{xz}=\alpha_{11}\cos(1,x)\cos(1,z)+\alpha_{22}\cos(2,x)\times\cos(2,z)+\alpha_{33}\cos(3,x)\cos(3,z). \quad (1)$$

Here α_{xz} is numerically equal to the x-component of the moment induced by a unit field in the z-direction, i.e., the xz-component of the polarizability tensor referred to the (x, y, z) system.

For the calculation of the second-order interaction it is also necessary to know the size of the dipoles associated with the nitro and aldehyde groups. Now the total moment of a dipole molecule is made up of the intrinsic moment belonging to the electrically asymmetric part and the induced moment which this produces in the (polarizable) remainder of the molecule. Calling the intrinsic moment ξ, the induced moment η and the total μ, we have the equation $\xi+\eta=\mu$, and also $\eta=\alpha\cdot\mathbf{F}$, where $\mathbf{F}$ is the field strength caused by ξ and α is the polarizability of the remainder. These equations may be solved simultaneously for ξ, taking the tensorial nature of α into account.

The nitro ξ was resolved along the two N−O bonds. Each ξ was allocated to the centroid of the corresponding group, for this is the centroid of positive charge, and that of negative charge must be close by.

The second-order interaction is conveniently expanded, for computation, in terms of the electric moments connected with transitions between the various energy levels. As London has shown,[2] the simple formulation is not valid for that portion which is expanded in terms of the rotational energies. This portion, however, makes up the dipole interaction and the induction effect of classical theory. The remainder of the second-order interaction energy is called the dispersion effect by London. The first two take the forms:

$$E_{\text{dip}}=-\frac{1}{R^3}[2\xi_x'\xi_x''-\xi_y'\xi_y''-\xi_z'\xi_z''] \quad (2)$$

and

$$E_{\text{ind}}=-\frac{1}{2R^6}[4\alpha_{xx}'\xi_x''^2+\alpha_{yy}'\xi_y''^2+\alpha_{zz}'\xi_z''^2]-\frac{1}{2R^6}[4\alpha_{xx}''\xi_x'^2+\alpha_{yy}''\xi_y'^2+\alpha_{zz}''\xi_z'^2]. \quad (3)$$

These interactions are computed for the three groups taken pair-wise, and the prime and second refer to the members of such a pair. The phenylene residue was considered to be dipole-free. The x-axis, of course, joins the centroids of the pair for which calculation is being made.

The dispersion effect demands a more thorough treatment. We have used Cartesian coordinates throughout, instead of the polars employed by London. His equation for the interaction in terms of the displacement components thus becomes

$$E_{00}^{(2)}=\frac{-e^4}{R^6}\sum_{k'l'}\left\{\frac{[2(X_1)_{0k'}(X_2)_{0l'}-(Y_1)_{0k'}(Y_2)_{0l'}-(Z_1)_{0k'}(Z_2)_{0l'}]^2}{E_{k'}-E_0+E_{l'}-E_0}\right\}. \quad (4)$$

Here, for example, the x-component of the displacement associated with the transition $O\rightarrow k'$ in group 1 is represented by $e(X_1)_{0k'}$. $E_{00}^{(2)}$ is the dispersion interaction, i.e., the second-order shift of the ground state expanded in terms of those transitions for which the system is originally in the ground state at room temperatures. R is the intercentroid distance. It will be seen that k' is a variable quantum number for group 1, as is l' for group 2. Each denominator is the sum of the energies of the corresponding transitions.

When the square is expanded, the numerators become

$$(4X_1^2X_2^2+Y_1^2Y_2^2+Z_1^2Z_2^2+2Y_1Y_2Z_1Z_2-4X_1X_2Y_1Y_2-4X_1X_2Z_1Z_2). \quad (5)$$

The quantum numbers are understood, having been omitted for compactness. Such electric moments can in principle be evaluated quantum-mechanically, but it is preferable to make use of the relation

with the polarizability $\mathbf{m}=\alpha\cdot\mathbf{F}$; whereby sums of the unknown displacement components may be replaced by known polarizability components. Consider for example α_{xz}, again the x-component of the displacement induced by a unit field in the z-direction.

The eigenfunction of a group perturbed by a field F_z is [4]

$$\psi=\psi_0-eF_z\sum_i\frac{\psi_i\int\tilde{\psi}_i z\psi_0 d\tau}{E_i-E_0}. \tag{6}$$

Multiply both sides by $\tilde{\psi}ex$ and integrate over configuration space:

$$e\int\tilde{\psi}x\psi d\tau=e\int x\left(\tilde{\psi}_0-eF_z\sum_i\frac{\tilde{\psi}_i\int\psi_i z\tilde{\psi}_0 d\tau}{E_i-E_0}\right)\left(\psi_0-eF_z\sum_i\frac{\psi_i\int\tilde{\psi}_i z\psi_0 d\tau}{E_i-E_0}\right)d\tau. \tag{7}$$

The first parenthesis is $\tilde{\psi}$ written in full. Performing the indicated multiplication:

$$e\int\tilde{\psi}x\psi d\tau=e\left[\int\tilde{\psi}_0 x\psi_0 d\tau-eF_z\sum_i\frac{\int\tilde{\psi}_0 x\psi_i d\tau\int\tilde{\psi}_i z\psi_0 d\tau}{E_i-E_0}-eF_z\sum_i\frac{\int\tilde{\psi}_i x\psi_0 d\tau\int\tilde{\psi}_0 z\psi_i d\tau}{E_i-E_0}+\cdots\right]. \tag{8}$$

The first term in brackets is the energy of the ground state, and it can be made to vanish by convention. The left side is the x-component of displacement produced by F_z. Accordingly, with the previous notation for matrix components of displacement:

$$\alpha_{xz}=-2e^2\sum_i[X_{0i}Z_{0i}/(E_i-E_0)]. \tag{9}$$

Finally, by selecting an effective average energy V for the denominators of our various expressions one obtains

$$E_{00}^{(2)}=-\frac{V}{8R^6}[4\alpha_{xx}'\alpha_{xx}''+\alpha_{yy}'\alpha_{yy}''+\alpha_{zz}'\alpha_{zz}''+2\alpha_{yz}'\alpha_{yz}''-4\alpha_{xy}'\alpha_{xy}''-4\alpha_{xz}'\alpha_{xz}'']. \tag{10}$$

This V was empirically found, in the cases investigated by London,[2] to lie near to the ionization potential of the groups involved. Accordingly, 12 v.e. were used in the present work. A more accurate determination could be made by integrating the measured absorption of the groups, but the necessary data are not at hand. The method of Mayer[5] might be used or the actual spectrum, appropriately plotted, might be planimetered.

The values of R were read from a diagram of the molecule, drawn to scale. Centroids were found by graphic statics. The aromatic C−C distance was assumed to be 1.42A, and the others were made up from Pauling's table.[6] All valence angles were assumed tetrahedral except O−N−O. Following Kohlrausch[7] this is taken to be 103°.

[4] Sommerfeld, *Wellenmechanischer Ergänzungsband*, p. 173, Vieweg, Braunschweig, 1929.
[5] Mayer, J. Chem. Phys. **1**, 270 (1933).
[6] Pauling, Proc. Nat. Acad. **18**, 293 (1932).
[7] Kohlrausch, *Der Smekal-Raman-Effekt*, p. 194, Berlin, 1930.

The sum of the dipole, induction, and dispersion effects is then calculated for a number of orientations and plotted in Fig. 1. The equilibrium configuration, represented by the lowest point, is that for which the molecule is coplanar. The lowest pass is seen to be that connecting successive equilibria of the nitro group.

Any attempt to rotate the aldehyde group more than about 90° would produce large repulsions in addition to those shown on the diagram because of steric hindrance between the oxygens of the nitro and aldehyde groups. In any case, it seems probable that in 2,4,6-trinitrobenzaldehyde the aldehyde group stands more or less perpendicular to the plane of the ring as a result of interaction with nitro groups on both sides of it.

The pass for the ortho compound has a height of 1380 cal./mol., i.e., 2.4 RT. In consequence, the rotation will be greatly hindered, but not altogether eliminated. For the tri-substituted

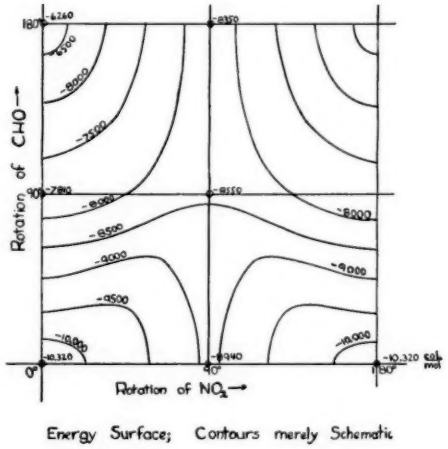

FIG. 1. Altitude, energy of o-nitrobenzaldehyde; abscissa, angular rotation of nitro; ordinate, angular rotation of aldehyde.

compound, rotation of the nitro groups should be fairly easy. If the ortho compound is treated by the method discussed by Pauling,[8] the motion of the nitro group is seen to be that of a quantized torsional oscillator, with the lower levels separated by about one-fifteenth of the height of the potential barrier. Half of the molecules will be found in the lowest four vibrational levels, and about ten percent will be rotating. As the vibrational energy of the nitro group is gradually increased from zero, the periods start with $\pi/(V/I)^{\frac{1}{2}}=3.27\times10^{-13}$ sec. for the lowest level and go to infinity when the energy is just equal to the height of the potential barrier, $2V$. I is the moment of inertia of the nitro group, determined by graphic statics. Beyond this unstable equilibrium, more energy will cause rotation, at first with a very long period, then more rapidly, until the rotation approximates that of an unhindered rotator. The periods for most of the rotating molecules lie between 10^{-12} and 10^{-13} sec.

ENERGY TRANSFER, DEACTIVATION AND REACTION

The third question mentioned in the opening paragraph must unfortunately be treated with still less exactitude. It was stated that the actinic radiation is absorbed in the nitro group, presumably by the electrons of the N−O bonds. With the molecule constrained to a flat configuration, the observed quantum efficiency of one-half could be very simply explained by saying that light absorbed by the bond more distant from the aldehyde is lost; whereas light absorbed by the bond nearer the aldehyde causes reaction. This, however, neglects the possibility of a transfer of activation between the two bonds, as well as the possibility of some deactivation in the proximal bond, and a more detailed consideration is required.

We may assume that energy is absorbed by a virtual oscillator in one or the other of the bonds. Let us call the state of the system in which the distal bond is excited ψ_1, and the state in which the proximal bond is excited ψ_2. The virtual oscillator perturbs the other bond. Then if it were impossible for the group ever to lose its energy, the latter would resonate between the two bonds, and the state of the system at any time would be given by a superposition[9]

$$\psi=c_1\psi_1+c_2\psi_2.$$

In such a case the c's would be undamped periodic functions of the time, or, according to the quantum-mechanical view, the absolute square of c_i at a given instant would give the probability of finding the energy in ψ_i.

This transfer process is very like that studied by Kallmann and London.[10] Indeed, an evaluation of the probability by the standard theory of coupled vibrations gives their Eq. (32). We shall write this equation in the form

$$|c_2|^2=\sin^2(2\pi p^2t/hR^3), \qquad (11)$$

for the case in which ψ_1 is originally excited at a time t before c_2 is being evaluated. The other symbols have the following definitions: p^2 is the square of the average absolute magnitude of the moment of the virtual oscillator produced by the absorption of radiation, h is Planck's constant, and R is the effective distance between 1 and 2. The latter is taken as 2.1A, the intercentroid distance of the two nitro bonds, and the former is found from the experimentally determined

[8] Pauling, Phys. Rev. **36**, 440 (1930).

[9] Dirac, *Quantum Mechanics*, pp. 18, 162, Oxford, 1930.

[10] Kallmann and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

effective cross section for absorption, by using the formula[11]

$$p^2 = 3cha/8\pi^2\nu. \qquad (12)$$

Here c is the velocity of light, a is the effective cross section per unit time for absorption, and ν is the incident frequency. For 3660A, a is 2.4×10^{-4} cm²/sec., and is found by easy transformations from the observed molecular extinction coefficient. The meaning of this value is that if a layer of molecules of o-nitrobenzaldehyde is exposed, each to a quantum of 3660A radiation, then on the average 2.4 out of every 10^4 quanta will be absorbed.

The least value of t in Eq. (11) for which the argument of the $\sin^2$ goes to $\pi/2$, and hence for which $|c_2|^2$ goes to unity, is 2.2×10^{-13} sec. This time will be denoted by T_1 and called the time of transfer. Accordingly,

$$T_1 = \hbar R^3/p^2 = 2.2\times10^{-13} \text{ sec.} \qquad (13)$$

Deactivation by the remainder of the molecule and by the surrounding solvent molecules occurs by a similar process, but more rapidly. The effective distance to the surrounding molecules is indeed greater than to the other nitro bond, and, other things being equal, the time varies with the cube of this. Kinetic theory molecular diameters are usually about 3.5A. On the other hand, the unexcited nitro bond obscures a relatively small solid angle, perhaps one-tenth of a sphere surrounding the excited one. Thus the time of deactivation will be approximately

$$T_2 = T_1(1/10)(3.5/2.1)^3 \backsimeq 10^{-13} \text{ sec.} \qquad (14)$$

It is assumed that the quasi-static polarizability, which conditions p, is of the same order for the surroundings as it is for the nitro bond.

No strictly analogous time can be given for the reaction process because of the different mechanism involved. Should the probability of reaction per unit time depend merely on the probability of finding the molecule still in the initial state for $|c_2|^2=1$ at $t=0$, then one might expect the curve of probability/time to behave like $1-e^{-t}$. However, this means that the rate of reaction is greatest at $t=0$. If, on the other hand, the reaction always takes a finite time, then the curve will possess a toe, as does the graph of $\sin^2 t$. Thus for a short interval near $t=0$, the curve will resemble that for transfer, except that the probability will approach unity asymptotically rather tangentially.

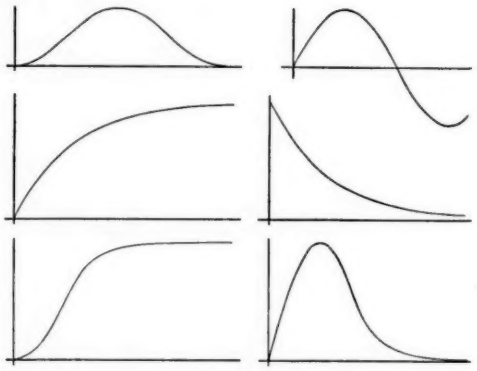

FIG. 2. Type curves. The left column contains $W=\sin^2 t$, $W=1-e^{-t}$, and a composite curve. The scales are arbitrary. The right column contains the time derivatives of these curves in the same order.

A similar conclusion holds for the deactivation process; since activation transferred to an acetone molecule stands little chance of returning to the nitro bond. The derivative curve, expressing the rate of deactivation of reaction, will be the derivative of $\sin^2 x$ at the start, i.e., $\sin 2x$, and e^{-x} at the end. The two may be multiplied or fitted as are the two wave functions in the process of finding a self-consistent field (Fig. 2). Since for all three processes, the curves are similar for a considerable time, we may allot a time T_3 to the reaction process on the same footing as the others. An evaluation of this is pure guesswork, but it is no doubt of the order of a few vibration periods, say 10^{-13} sec. also.

We shall assume that the processes of transfer, deactivation, and reaction are independent, i.e., that only one of them is occurring in any one molecule at any given time. This corresponds to assuming that the absorbed quantum retains its identity as long as it remains an electromagnetic phenomenon. In order for the excitation energy to be degraded and finally lost as heat, it must go over to relative motional energy of different systems. This can occur by a coupling between electronic and nuclear vibrations within one molecule and a dissipation of the resulting vibrational energy by collisions. This degradation is presumably rather slow on the whole, because of the great disparity between the masses of the

[11] Reference 9, p. 232 inf.

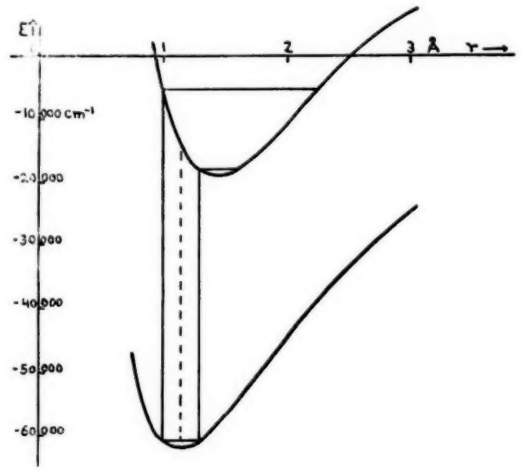

FIG. 3. Morse curves for nitric oxide, showing the bond extension following the absorption of light. A similar effect may occur in the nitro group.

nuclei and the electrons and the resulting large number of vibrations required to transfer the energy. However, one may expect that a certain amount of the excitation goes into vibrational energy at once if the higher state is an upper vibrational level of the electronically excited bond.

The spectrum of o-nitrobenzaldehyde has not been analyzed, but that of NO has. The Morse curves for the ground state and the excited state which gives the β-bands may be plotted from the data so obtained[12] (Fig. 3). They show that light absorption by molecules at room temperature yields molecules having a few Cal. of vibrational energy, with a maximum internuclear distance considerably greater than that of the ground state. That a similar situation exists for the nitro group seems plausible.

The nitro group, of course, has three fundamental vibrations, and the sudden extension of one of its bonds corresponds to the excitation of all three modes, but principally the unsymmetrical valence vibration and the deformation vibration are excited, in the proportion of about two to one, as may be seen from a diagram of the molecule and a consideration of the various restoring forces. There will not be time for appreciable transfer of this vibration from one bond to the other, especially if 2 is the excited one, but in the latter case the vibration may well be important in causing the reaction. If the rest of the molecule remained rigid, the vibrational motion would swing the oxygen nucleus near enough to the aldehyde hydrogen so that an hydroxyl group with normal nuclear separation could form by a mere redistribution of the electron cloud (Villars' allegiance exchange). At the same time a chemically saturated nitroso group could form from the remainder of the nitro group, leaving the hydroxyl to react with the carbonyl.

The actual process probably does not fall into steps, but is a continuous shift of the oxygen from one group to the other, expressible in the Eyring manner. However, it may well be that the molecule must oscillate into a favorable position to cross the energy barrier, so that T_3 is taken as 10^{-13} sec. rather than as some shorter time.

It seems fair to assume that the relative frequency of deactivation and reaction is the ratio of the rates of the two processes considered separately. Since there is one chance in two that the activated system is initially in ψ_1 and the like for ψ_2, the probability of reaction may be expressed as $\frac{1}{2}(P_1+P_2)$, where P_1 is the probability of reaction if the system is originally in the state ψ_1 and P_2 is the probability of reaction if the system is originally in ψ_2. In the second case, the probability is the partition coefficient for the separation of excited molecules into the reacted or deactivated forms. The latter group includes those molecules in which transfer of activation to 1 occurs, for energy, one transferred from 2, has a negligible chance of causing reaction. The rate of reaction from ψ_2 is the ratio of the slopes of the graphs of probability against time. Near $t=0$, for example, it is

$$\frac{2}{T_3}\sin\frac{2t}{T_3}\Big/\left(\frac{2}{T_1}\sin\frac{2t}{T_1}+\frac{2}{T_2}\sin\frac{2t}{T_2}\right). \quad (15)$$

The average of P_2 during a short interval a is then, by the standard formula,

$$P_2=\frac{\int_0^a\left[\sin\frac{2t}{T_3}\Big/\left(\frac{1}{T_1}\sin\frac{2t}{T_1}+\sin\frac{2t}{T_2}\right)\right]dt}{\int_0^a dt}. \quad (16)$$

[12] International Critical Tables, 5, 415, 417 (1929).

The terms in T_2 and T_3 change to exponentials after about 0.8×10^{-13} sec., as noted above. This expression is most conveniently handled graphically. Analogously,

$$P_1=\frac{\int_0^a\left(\frac{1}{T_1}\sin\frac{2t}{T_1}\Big/\sin\frac{2t}{T_2}\right)dt}{\int_0^a dt}\cdot P_2.$$

That is, there is a partition of the energy into deactivation and transfer, and then, in the transferred portion, a further partition expressed by P_2.

Graphical integration gives $P_2=0.80$, $P_1=0.20$. Since ψ_1 and ψ_2 are equally probably *a priori*, the quantum efficiency is the arithmetical mean of these, namely $\Phi=0.50$, exactly as found experimentally.

This result is rather surprising at first; a further inspection shows it to come from the assumption that $T_2=T_3$, and, from other assumptions made above. It might have been assumed at the start that Φ has the experimental value and that T_2 and T_3 are to be adjusted accordingly. Assuming a different value for T_1 without changing the others will not change Φ, the quantum efficiency, but only the relative values of P_1 and P_2.

Of course, T_2 and T_3 may change in different manners with change in temperature. In particular, rising temperature probably increases T_3 by throwing a considerable fraction of the nitro groups into high states of torsional oscillation and rotation. Such molecules will spend most of their time in orientations unsuitable for reaction, and the temperature coefficient will accordingly be negative. Indeed, a negative temperature coefficient was actually found by Zimmer.[13]

The quantum efficiency $\Phi=0.67$ found in acetone solutions for 2,4,6-trinitrobenzaldehyde may be interpreted simply on the basis of the foregoing computations. As noted above, the contour map (Fig. 1) shows that the three vicinal groups cannot easily be coplanar. The aldehyde group is doubtless forced to within 30° or so of perpendicularity to the plane of the ring. In such a case, the nitro groups are no longer hindered by a very high potential barrier and can rotate somewhat, say with a period of about 10^{-13} sec. at room temperature. This is rapid enough so that all four bonds become more nearly equivalent than in the mono-substituted compound. That is, P_2 is the most important partition coefficient and $P_2>\Phi>0.5$. The lower quantum efficiencies found for this compound in ligroin solution and in the solid state may be due either to a reduction in the amount of rotation or a reduction in P_2. Lower quantum efficiencies at shorter wave-lengths may in every case be plausibly assigned to an inner light filter effect of other portions of the molecule than those which can be active in causing reaction, but may partly be caused by a decrease of T_2 for higher frequencies of exciting light.

Conclusion

A calculation of the position-sensitive interactions of the nitro and aldehyde groups in o-nitrobenzaldehyde indicates that at room temperature these groups will be for the most part constrained to a flat configuration, coplanar with the phenylene ring, and that rotation of the nitro group will precede that of the aldehyde group. A consideration of the possible processes following upon the absorption of a quantum of light in one of the N−O bonds leads to the conclusion that the observed quantum efficiency of one-half is due principally to an equality between times of deactivation and reaction. Most of the absorption in the proximal bond produces reaction; while most of the energy absorbed in the distal bond is lost by deactivation, and the yield is independent of energy transfer between the two bonds.

The explanation, although approximate in character, contravenes no accepted ideas on the structural arrangement of the molecule, and contravenes no physical principle. The description is still not complete; in particular it does not cover the Eyring diagram for the motion of the oxygen atom.

The authors wish to express their gratitude to Drs. W. V. Houston and F. Bloch for stimulating conversations on this problem as well as for specific assistance in certain instances.

[13] Zimmer, Zeits. f. physik. Chemie **B23**, 239 (1933).

On the Theory of Strong Electrolyte Solutions*

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The nature of the approximations involved in the derivation of the Poisson-Boltzmann equation of the Debye-Hückel theory is investigated in detail from the standpoint of classical statistical mechanics. The validity of the initial Debye approximation, under the restrictions originally imposed upon it, is confirmed. Deviations arising from fluctuation terms and van der Waals forces are roughly estimated. An alternative to the Bjerrum method for the treatment of ions of small size and high valence is outlined.

I.

ALTHOUGH the Debye-Hückel[1] theory furnishes a strikingly satisfactory account of many of the properties of strong electrolyte solutions, it is based upon physical assumptions, which, though plausible, are not in exact accord with the formal theory of statistical mechanics. This discrepancy has exposed the theory to a certain amount of adverse criticism in recent years. Although some of this criticism has certainly been of value in bringing the imperfections of the theory to light, none of it has been very successful in estimating their quantitative importance. It is the object of the present article to investigate in some detail the approximations involved in the derivation of the Debye-Hückel equations from statistical mechanics, and to estimate, insofar as possible, their quantitative importance.

The formulation of a statistical theory of electrolyte solutions offers little difficulty in itself. However, obstacles are immediately encountered in the evaluation of certain phase integrals. Until these are evaluated the theory remains formal and somewhat impotent. In order to obtain integrals, which can be treated with much hope of success, it is necessary to idealize the solvent as a continuous medium characterized only by its dielectric constant. Let us suppose that a solution of volume v consists of N ions dissolved in a solvent of dielectric constant D. Let F be the Helmholtz free energy, $E-TS$, of the solution when all ions bear their full charges $e_1, \cdots e_N$, and F_0 be the free energy when all ions are completely discharged. For convenience, we exclude from F a constant term of the form $\sum_{k=1}^{N} e_k^2/2Db_k$ arising from the self-energy of the ions. If we assume that the system of N ions, in thermal equilibrium with a temperature T, can be represented by a classical canonical ensemble, we may write

$$e^{-\beta(F-F_0)} = Z_N/Z_N^\circ,$$

$$Z_N = \int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_N, \qquad (1)$$

$$Z_N^\circ = \int \cdots \int e^{-\beta U_N} dv_1 \cdots dv_N,$$

where β is equal to $1/kT$, V_N is the mutual potential energy of the fully charged ions, and U_N is the mutual potential energy of the completely discharged ions, consisting only of the terms in V_N, arising from short range van der Waals forces. Integration in the configuration space v_k of each ion is to be extended over the volume, v, occupied by the solution.

The position of any ion k can be specified by a set of configuration coordinates, q_k, for example the three components of a vector $\mathbf{r}_k$, drawn from some arbitrary origin and terminating at the center of the ion k. For simplicity we assume that the ions have no internal degrees of freedom, and that they are spherically symmetrical. Their mutual potential energy may then be expressed as a function of the configuration coordinates $q_1 \cdots q_N$ in the following manner.

$$V_N = \tfrac{1}{2} \sum_{k=1}^{N} [e_k \psi_k(q_k) + U_k(q_k)],$$

$$\psi_k(q_k) = \sum_{\substack{l=1 \\ \neq k}}^{N} \frac{e_l}{D\,|\mathbf{r}_l - \mathbf{r}_k|}, \qquad (2)$$

$$U_k(q_k) = \sum_{\substack{l=1 \\ \neq k}}^{N} u_{kl}(|\mathbf{r}_k - \mathbf{r}_l|),$$

* No. 334.

[1] Debye and Hückel, Phys. Zeits. **24**, 185, 305 (1923).

where e_k is the charge on an ion k, and $|\mathbf{r}_l-\mathbf{r}_k|$ is the distance between the ion pair k and l. Thus $\psi_k(q_k)$ is the electrostatic potential produced in the interior of the ion k by the charges on the other ions. The potential of the short range van der Waals and polarization forces can be represented to a very close approximation, as in the theory of imperfect gases, by a sum of terms of the type u_{kl}, each depending only upon the relative coordinates of the ion pair k and l.

Eq. (1) is of course purely formal and is of little value unless it is possible to evaluate the phase integrals Z_N and Z_N°. The integral Z_N°, involving only short range van der Waals forces, may be obtained by the methods employed in the statistical theory of imperfect gases. This method is not applicable in the case of Z_N, which unfortunately is very difficult to treat. Kramers[2] has attempted to evaluate Z_N and van Rysselberghe,[3] using a similar method, has attempted to calculate the osmotic pressure directly without the intermediate calculation of Z_N. Both methods are based upon dimensional considerations, which fail to account satisfactorily for the rôle of the van der Waals forces between the ions. Moreover, unless these forces, which determine the size of the ions, are taken into account, Z_N clearly diverges. Thus, while very ingenious, the investigations of both Kramers and van Rysselberghe fail to do much more than confirm the Debye-Hückel limiting law at low concentrations, without indicating how a better approximation may be obtained.

Instead of basing the calculation of the free energy F on a direct determination of Z_N, it is possible to start from the mean electrostatic potential in an ion, defined as follows:

$$\bar{\psi}_k=\frac{\int\cdots\int\psi_k(q_k)e^{-\beta V_N}dv_1\cdots dv_N}{\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_N}. \tag{3}$$

From (1), it is easily demonstrated that

$$\begin{aligned}\partial F/\partial e_k&=\bar{\psi}_k, &\text{(a)}\\ \partial\bar{\psi}_k/\partial e_l&=\partial\bar{\psi}_l/\partial e_k. &\text{(b)}\end{aligned} \tag{4}$$

These relations have been derived and discussed in detail by Onsager[4] and later by Halpern.[5] If the charges on the ions are varied in an arbitrary manner, we have from (4a)

$$\delta F=\sum_{k=1}^{N}\frac{\partial F}{\partial e_k}\delta e_k=\sum_{k=1}^{N}\bar{\psi}_k\delta e_k. \tag{5}$$

From (4b), the condition of integrability, we may conclude that the integral of δF in any charging process depends only upon the initial and final values of the charges, and not upon the method of charging. Thus the difference $F-F_0$, where F is the free energy of the solution when all ions have the full charges $e_1\cdots e_N$, and F_0, the free energy when all ions are completely discharged, may be obtained by integrating $\sum_{k=1}^{N}\bar{\psi}_k\delta e_k$ along any path. The Debye charging process is the one most commonly employed. In this process, all ions are charged simultaneously by equal fractions of their final charge, so that

$$F-F_0=\sum_{k=1}^{N}\int_0^1 e_k\overline{\psi_k(\lambda e_1,\cdots\lambda e_N)}d\lambda. \tag{6}$$

It is often possible to assume that F_0 is the free energy of an ideal solution, or when this is not permissible to treat it by empirical methods, applicable to ordinary non-electrolyte solutions. It is to be emphasized that the charging process need not be attributed physical significance, but can be regarded simply as a mathematical device for calculating the free energy function, F, defined by Eq. (1). The method outlined here, although somewhat indirect, has distinct advantages, since it is easier to calculate $\bar{\psi}_k$, at least approximately, than it is to calculate Z_N.

II.

The foundation for a precise statistical calculation of $\bar{\psi}_k$, the mean potential produced in an ion k, by the other ions in the solution, was laid by Fowler.[6] We shall have occasion to use the mean Poisson equation of Fowler's theory, Eqs. (582) and (584), which we derive here in a slightly different and somewhat more direct manner. From this point on, we depart from Fowler, employing a method of treating the statistical space

[2] H. A. Kramers, Proc. Amst. Acad. Sci. **30**, 145 (1927).
[3] P. van Rysselberghe, J. Chem. Phys. **1**, 205 (1933).
[4] Onsager, Chem. Rev. **13**, 73 (1933).
[5] Halpern, J. Chem. Phys. **2**, 85 (1934).
[6] R. H. Fowler, *Statistical Mechanics*, 8.7, 8.8, Cambridge University Press (1929).

charge around an ion, which leads to somewhat more concrete results.

We begin by considering the electrostatic potential at some fixed point, q, in the solution

$$\psi(q)=\sum_{l=1}^{N}(e_l/D|\mathbf{r}_l-\mathbf{r}|), \tag{7}$$

where $|\mathbf{r}_l-\mathbf{r}_k|$ is the distance of the lth ion from the point q. The mean value of $\psi(q)$, when a selected ion k is fixed at a point q_k is given by

$$\overline{{}^{k}\psi(q)}=\frac{\int\cdots\int\psi(q)e^{-\beta V_N}dv_1\cdots dv_{N-1}}{\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_{N-1}}, \tag{8}$$

where the integrations are extended over the coordinates of all ions except those of the selected ion, k. We define $\psi_k(q)$ as the potential at q, arising from all ions except the fixed ion k.

$$\psi_k(q)=\psi(q)-e_k/D|\mathbf{r}-\mathbf{r}_k|. \tag{9}$$

The term $e_k/D|\mathbf{r}-\mathbf{r}_k|$ is a constant as long as ion k remains fixed, and is unaffected by a mean value operation of the type (8). Suppose that $\overline{{}^{k}\psi_k(q)}$ has been determined everywhere in the neighborhood of the ion k, and let $\overline{{}^{k}\psi_k(q_k)}$ be its value in the interior of the ion k. From Eqs. (3) and (8) we obtain the relation

$$\frac{\int\overline{{}^{k}\psi_k(q_k)}[\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_{N-1}]dv_k}{\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_N}=\bar{\psi}_k. \tag{10}$$

If $\overline{{}^{k}\psi_k(q_k)}$ is independent of q_k, we may write immediately

$$\overline{{}^{k}\psi}_k=\bar{\psi}_k. \tag{11}$$

We may assume without formal proof that $\overline{{}^{k}\psi}_k$ is independent of q_k, that is, of the position of k relative to the boundaries of the solution, except in a surface region of negligible volume. Otherwise direct contradictions with experiment would result, such as concentration gradients in the bulk of the solution. Therefore Eq. (11) may be accepted as valid, except for a quantity of negligible order.

We may rewrite Eq. (8), which defines $\overline{{}^{k}\psi(q)}$, in a somewhat different manner.

$$\begin{aligned}\overline{{}^{k}\psi(q)}&=\sum_{\substack{l=1\\ \neq k}}^{N}\int\frac{\overline{{}^{k}\rho_l(q_l)}}{D|\mathbf{r}_l-\mathbf{r}|}dv_l+\frac{e_k}{D|\mathbf{r}_k-\mathbf{r}|},\\ \overline{{}^{k}\rho_l(q_l)}&=e_l\frac{\int\cdots\int e^{-\beta[V_{N-1}+V_l(q_l)]}dv_1\cdots dv_{N-2}}{\int\cdots\int e^{-\beta V_N}dv_1\cdots dv_{N-1}}.\end{aligned} \tag{12}$$

In the expression for $\overline{{}^{k}\rho_l(q_l)}$, the coordinates of both k and l remain fixed in the integral in the numerator, while only those of k remain fixed in the integral in the denominator. For clearness we have expressed V_N as a sum of two terms, V_{N-1}, which is independent of q_l, and $V_l(q_l)$ which is given by

$$V_l(q_l)=e_l\psi_l(q_l)+U_l(q_l).$$

This is merely a rearrangement of terms, which may be carried out for any one of the N ions. Eq. (12) is precisely the solution of the following Poisson equation:[7]

$$\nabla^2\overline{{}^{k}\psi(q)}=-(4\pi/D)\overline{{}^{k}\rho(q)},$$

[7] The passage from (12) to (13) follows from a well-known transformation in potential theory, depending upon the fact that $\nabla^2|\mathbf{r}_l-\mathbf{r}|^{-1}$ is zero except when $\mathbf{r}_l=\mathbf{r}$, where it has a singularity. Thus in any integral of the form

$$\int F(q_l)\nabla^2|\mathbf{r}_l-\mathbf{r}|^{-1}dv_l$$

$$\overline{{}^{k}\rho(q)} = \sum_{l=1}^{N} e_l \frac{\int \cdots \int e^{-\beta[V_{N-1}+V_l(q)]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_{N-1}}. \tag{13}$$

In general, there will be several ion types present in the solution. If N_i be the number of ions of the ith type, N_i/v is the bulk concentration C_i of that type. Moreover, $\overline{{}^{k}\rho_l(q)}$ is the same function $\overline{{}^{k}\rho_i(q)}$ for all ions of the ith type. Therefore we may write

$$\overline{{}^{k}\rho(q)} = \sum_i c_i e_i \zeta_{ki}(q),$$

$$\zeta_{ki}(q) = \frac{v\,\overline{{}^{k}\rho_i(q)}}{e_i} = \frac{v \int \cdots \int e^{-\beta[V_{N-1}+V_i(q)]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_{N-1}} \tag{14}$$

and the Poisson Eq. (13) becomes $\Delta^2 \overline{{}^{k}\psi(q)} = -(4\pi/D)\sum_i c_i e_i \zeta_{ki}(q)$, (15)

where the sum is extended over all ion types. Properly, the selected ion k should be omitted from the sum, but its omission would alter the concentration of the type to which it belongs by a quantity of the order C_i/N_i, which can be ignored altogether.

It is sometimes convenient to define a function V_{ki} by means of the following relation

$$e^{-\beta V_{ki}} = \zeta_{ki}. \tag{16}$$

It may be shown that V_{ki} is the potential of the mean force acting on the ion i at the point q.[4] When the ζ_{ki} are expressed in the form (16), Eq. (15) becomes identical in form with Fowler's Eqs. (583) and (584). From Eqs. (14) and (16) one obtains by differentiation of ζ_{ki}

$$\nabla^2 V_{ki} + 4\pi e_i \rho_{ki}/D = -\beta[\overline{{}^{ik}(\nabla V_i)^2} - (\nabla V_{ki})^2],$$

$$\rho_{ki} = -\frac{D}{4\pi e_i} \overline{{}^{ik}\nabla^2 V_i}, \tag{17}$$

where the mean values are taken with the ion i fixed at the point q and the ion k fixed at the point q_k. Eq. (17) is identical with Fowler's Eqs. (585) and (586). If the quantities ρ_{ki} and $\overline{{}^{ik}(\nabla V_i)^2}$ were known, $\overline{{}^{k}\psi(q)}$ could be determined by the simultaneous solution of Eqs. (15), (16), and (17) with appropriate boundary conditions. Unfortunately, we do not have the necessary information about ρ_{ki} and $\overline{{}^{ik}(\nabla V_i)^2}$, nor does there seem to be any practicable means of obtaining it. For this reason, we prefer to study the charge density $\overline{{}^{k}\rho(q)}$ of Eq. (14) by another method, which utilizes the properties of the functions ζ_{ki} themselves and not those of their derivatives.

The familiar Poisson-Boltzmann equation of the Debye-Hückel theory follows immediately from Eqs. (15) and (16) when $e_i \overline{{}^{k}\psi(q)}$ is substituted for V_{ki} in ζ_{ki}. This is admittedly an approximation, for it involves the assumption that the potential of the mean force is equal to the mean potential. However, the approximation

$$V_{ki} = e_i \overline{{}^{k}\psi(q)} \tag{18}$$

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the integrand is zero except in the immediate neighborhood of the point $\mathbf{r}_l = \mathbf{r}$. The integral in the vicinity of this point may be transformed by Green's theorem and evaluated as $J = -4\pi F(q)$. This may be represented symbolically by saying that $\nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1}$ is a delta-function

$$\nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1} = -4\pi\delta(\mathbf{r}_l - \mathbf{r}),$$

where $\delta(\mathbf{r}_l - \mathbf{r})$ has the property

$$\int F(q_l)\delta(\mathbf{r}_l - \mathbf{r}) dv_l = F(q).$$

Thus the $\rho(x)$ in the integrand of Fowler's Eq. (584) is simply

$$-4\pi \sum_{\substack{l=1 \\ \neq k}}^{N} \delta(\mathbf{r}_l - \mathbf{r}).$$

is by no means as objectionable as the approximation attributed to Debye and Hückel by Fowler (*Statistical Mechanics*, Eq. (587))

$$\nabla^2 V_{ki} = -(4\pi e_i/D)\,{}^k\overline{\rho(q)} = e_i\nabla^2\,{}^k\overline{\psi(q)}. \tag{19}$$

Thus two functions may be approximately equal over a large interval even though their second derivatives are not. The approximate validity of (18), for example at large distances from the selected ion k, is not subject to the validity of (19) nor would it even follow from (19), unless all boundary values of the two functions $e_i\,{}^k\overline{\psi(q)}$ and V_{ki} were equal.

Fowler's criticism of the Debye-Hückel theory was based upon Eqs. (17) and (19). In order for these equations to be consistent it is necessary that $\beta[{}^{ik}\overline{(\nabla V_i)^2} - (\nabla V_{ki})^2] + 4\pi e_i\rho_{ki}/D$ be equal to $4\pi e_i\,{}^k\overline{\rho(q)}/D$. If ρ_{ki} and ${}^k\overline{\rho(q)}$ were approximately equal, the fluctuation in the force acting upon the ion i would have to be small. However, it turns out that this requirement is not necessary, for ρ_{ki} is quite different from ${}^k\overline{\rho(q)}$ and always much smaller. As Onsager[4] has pointed out Eq. (17) is meaningless, unless van der Waals forces of the repulsive type are taken into account. By the method employed in the derivation of Eq. (13), it is readily shown[8] that these repulsive forces, which give the ions their finite size, cause the Coulomb contribution to ρ_{ki} to vanish. Thus Eq. (17) should actually be written in the following manner:

$$-\beta[{}^{ik}\overline{(\nabla V_i)^2} - (\nabla V_{ki})^2] = \nabla^2 V_{ki} - {}^{ik}\overline{\nabla^2 U_i}, \tag{17a}$$

where $U_i(q)$ is the potential of the short range forces acting upon the ion i. This circumstance makes it even more difficult to determine whether Eqs. (17) and (19) are consistent, but it removes the restriction that the fluctuation in the force must be small. Finally, when it is emphasized that Debye and Hückel wished to obtain a differential equation for ${}^k\overline{\psi(q)}$, not V_{ki}, and that their result follows directly from Eqs. (15) and (18), it becomes clear that the adequacy of their approximation should not be judged on the basis of Eq. (19). Thus to conclude that the two functions V_{ki} and $e_i\,{}^k\overline{\psi(q)}$ could not be approximately equal in an extensive region of the solution simply because their second derivatives may not be equal, would to say the least, put the Debye-Hückel approximation in an unjustifiably unfavorable light.

III.

Solution of the Poisson Eq. (15) requires a knowledge of the mean charge density, ${}^k\overline{\rho(q)}$, which is expressible in terms of the functions ζ_{ki}. We shall now investigate the relation of these functions to

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[8] The density function ρ_{ki} in Eq. (17) is equal to $-\frac{D}{4\pi e_i}\,{}^{ik}\overline{\nabla^2 V_i(q)}$.

$${}^{ik}\overline{\nabla^2 V_i} = \frac{\int\cdots\int \nabla^2 V_i(q) e^{-\beta V_N(q_i=q)} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta V_N(q_i=q)} dv_1 \cdots dv_{N-2}}, \tag{a}$$

where the ions i and k remain fixed during the averaging process. Since

$$V_i(q) = e_i \sum_{\substack{l=1 \\ \neq i}}^{N} \frac{e_l}{D|\mathbf{r}_l - \mathbf{r}|} + U_i(q), \tag{b}$$

we may write (see reference 7)

$$\nabla^2 V_i = -\frac{4\pi e_i}{D} \sum_{\substack{l=1 \\ \neq i}}^{N} e_l \delta(\mathbf{r}_l - \mathbf{r}) + \nabla^2 U_i. \tag{c}$$

Thus

$${}^{ik}\overline{\nabla^2 V_i} = -\frac{4\pi e_i}{D} \sum_{\substack{l=1 \\ \neq i}}^{N} e_l \frac{\int\cdots\int e^{-\beta V_N(q_l=q_i=q)} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta V_N(q_i=q)} dv_1 \cdots dv_{N-2}} + {}^{ik}\overline{\nabla^2 U_i}. \tag{d}$$

Now due to van der Waals forces V_N contains terms of the form $u_{il}(q_i - q_l)$. Whenever any $|q_i - q_l|$ becomes zero as for example when $q_i = q_l = q$, there is always a term which becomes positively infinite and makes $e^{-\beta V_N(q_i=q_l)}$ vanish. Thus the first term of (d), arising from electrostatic forces, always vanishes and we are left with

$$\rho_{ki} = -(D/4\pi e_i)\,{}^{ik}\overline{\nabla^2 U_i}. \tag{e}$$

the mean potential ${}^{k}\overline{\psi(q)}$. The method to be employed is in certain respects similar to a general method proposed by Onsager.[4] We differentiate ζ_{ki} with respect to e_i, the charge on the ion i. Remembering Eqs. (2) and (14), we obtain

$$\frac{\partial \zeta_{ki}}{\partial e_i} = -\beta \zeta_{ki}[{}^{ik}\overline{\psi_i(q)} - {}^{k}\overline{\psi_i(q_i)}], \tag{20}$$

$${}^{k}\overline{\psi_i(q_i)} = \frac{\int\cdots\int \psi_i(q_i) e^{-\beta V_N} dv_1 \cdots dv_{N-1}}{\int\cdots\int e^{-\beta V_N} dv_1 \cdots dv_{N-1}}, \qquad {}^{ik}\overline{\psi_i(q)} = \frac{\int\cdots\int \psi_i(q) e^{-\beta[V_{N-1}+V_i(q)]} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+V_i(q)]} dv_1 \cdots dv_{N-2}}. \tag{21}$$

Thus ${}^{ik}\overline{\psi_i(q)}$ is the mean value of the potential at the point q, when the ion i is fixed at that point, and the ion k is fixed at the point q_k. The subscript i in $\psi_i(q)$ means as before that the term, $e_i/D|\mathbf{r}_i - \mathbf{r}|$ is omitted. For certain purposes it is convenient to express this potential in a somewhat different form. The mean potential at any point q', when the ions i and k are fixed at any points q_i and q_k is

$${}^{ik}\overline{\psi_i(q'; q_i, q_k)} = \frac{\int\cdots\int \psi_i(q') e^{-\beta V_N(q_i, \cdots q_k \cdots)} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta V_N(q_i, \cdots q_k \cdots)} dv_1 \cdots dv_{N-2}}. \tag{22}$$

The potential ${}^{ik}\overline{\psi_i(q)}$ is evidently equal to ${}^{ik}\overline{\psi_i(q; q, q_k)}$, that is the value of (22) when $q' = q_i = q$. Moreover it is clear that this latter potential must depend only on the relative coordinates $|q - q_k|$ of the ions i and k (except in the surface region of the solution). It therefore remains unaltered by an interchange of the coordinates of i and k, or by a shift of their center of gravity.

$${}^{ik}\overline{\psi_i(q; q, q_k)} = {}^{ik}\overline{\psi_i(q_i; q_i, q')}, \qquad |q - q_k| = |q' - q_i|, \tag{23}$$

so that one may write

$${}^{ik}\overline{\psi_i(q)} = \frac{\int\cdots\int \psi_i(q_i) e^{-\beta[V_{N-1}+V_k(q')]} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+V_k(q')]} dv_1 \cdots dv_{N-2}}, \tag{24}$$

subject to the condition that $|q' - q_i| = |q - q_k|$. We shall have occasion to use both of the alternative expressions (21) and (24) in discussing the properties of ${}^{ik}\overline{\psi_i(q)}$.

We may integrate Eq. (20) at once to obtain

$$\zeta_{ki} = \zeta_{ki}^{\circ} e^{-\beta \int_0^{e_i} {}^{ik}\overline{[\psi_i(q)}^{-}{}^{k}\overline{\psi_i(q_i)]} de_i}, \tag{25}$$

$$\zeta_{ki}^{\circ} = \frac{v \int\cdots\int e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q_i)]} dv_1 \cdots dv_{N-1}} = \frac{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \cdots dv_{N-1}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q_i)]} dv_1 \cdots dv_{N-1}}. \tag{26}$$

In the second equality (26), the v factor has simply been written as an integration over q_i. This can be done since the integrand $e^{-\beta[V_{N-1}+u_i(q)]}$ is independent of q_i, the running coordinates of the i ion having been replaced by q. It may be noted that ζ_{ki}° is formally the mean value, when $e_i = 0$, of the following function

$$\zeta_i^{\circ} = e^{-\beta[u_i(q) - u_i(q_i)]}; \qquad \zeta_{ki}^{\circ} = {}^{k}\overline{\zeta_i^{\circ}}\big|_{e_i=0}. \tag{27}$$

Substitution of (25) in Eq. (15) yields

$$\nabla^2 {}^{k}\overline{\psi(q)} = -\frac{4\pi}{D}\sum_i c_i e_i \zeta_{ki}^{\circ} e^{-\beta \int_0^{e_i} {}^{ik}\overline{[\psi_i(q)}^{-}{}^{k}\overline{\psi_i(q_i)]} de_i}. \tag{28}$$

This is an exact form of the Poisson equation for the mean potential ${}^{k}\overline{\psi(q)}$. We note that each of the ζ_{ki}° contains a factor $e^{-\beta u_{ki}(q - q_k)}$. When $|q - q_k|$ becomes small, van der Waals repulsion makes $u_{ki}(q - q_k)$ positively infinite and each ζ_{ki}° vanishes. Thus "inside" the ion k, the right-hand side of

Eq. (28) vanishes, and it becomes Laplace's equation. Outside of the ion k, the ζ_{ki}° are effectively unity except for a small term depending upon van der Waals forces. Without going into the details of the calculation, which would divert us from our main purpose, we may state that ζ_{ki}° is approximately given by[9]

$$\zeta_{ki}^{\circ}=1-2\sum_{j}B_{ij}C_j(\zeta_{kj}-1)+\cdots, \tag{29}$$

where the B_{ij} have the same form as the second virial coefficients of an imperfect gas, and C_j is the bulk concentration of the ion type j. If van der Waals forces of the attractive type are ignored and the ions are treated as rigid spheres, one may write

$$B_{ij}=(2\pi/3)a_{ij}^{3}, \tag{30}$$

where a_{ij} is the mean diameter of ions of types i and j.

We are chiefly interested in the properties of the mean potentials $^{ik}\overline{\psi_i(q)}$ and $^{k}\overline{\psi_i(q_i)}$. By means of the following identity, we can relate $^{ik}\overline{\psi_i(q)}$ to its values $^{ik}\overline{\psi_i(q)}\big|_{e_i=0}$ and $^{ik}\overline{\psi_i(q)}\big|_{e_k=0}$, when the charges on the ions i and k are, respectively, zero.

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[9] The function $\zeta_{ki}^{\circ}-1$ has the form

$$\zeta_{ki}^{\circ}-1=\frac{\int\cdots\int e^{-\beta V_{N-1}}[e^{-\beta u_i(q)}-e^{-\beta u_i(q_i)}]dv_1\cdots dv_{N-1}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q_i)]}dv_1\cdots dv_{N-1}}.$$

Making use of the identity

$$e^{-\beta u_i(q)}-e^{-\beta u_i(q_i)}=(e^{-\beta u_i(q)}-1)-(e^{-\beta u_i(q_i)}-1)$$

we may write

$$\zeta_{ki}^{\circ}-1=\frac{\int\cdots\int e^{-\beta V_{N-1}}[e^{-\beta u_i(q)}-1]dv_1\cdots dv_{N-1}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q_i)]}dv_1\cdots dv_{N-1}}$$
$$-\frac{\int\cdots\int e^{-\beta V_{N-1}}[e^{-\beta u_i(q_i)}-1]dv_1\cdots dv_{N-1}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q_i)]}dv_1\cdots dv_{N-1}}.$$

Now $U_i(q)=\sum_{j=1,\neq i}^{N}u_{ij}(q_j-q)$, where the potentials, $u_{ij}(q_j-q)$, of the short range forces are effectively zero unless the distance $|\mathbf{r}_j-\mathbf{r}|$ is very small, of the order of a molecular diameter. Thus $e^{-\beta u_i(q)}-1$ is zero unless at least one distance $|\mathbf{r}_j-\mathbf{r}|$ is of the order of a molecular diameter. Likewise $e^{-\beta u_i(q_i)}-1$ is zero unless at least one interionic distance $|\mathbf{r}_j-\mathbf{r}_i|$ is of the order of a molecular diameter. Thus each of the two parts of $\zeta_{ki}^{\circ}-1$ must at least contain the ionic concentration C to a power not lower than the first, and we may state at once $\zeta_{ki}^{\circ}-1=0(C)$ that is, $\zeta_{ki}^{\circ}-1$ is of negligible order if we neglect terms involving the first power of the concentration. However, we can go farther than that. Thus we may write

$$e^{-\beta u_i(q)}=\prod_{\substack{j=1\\ \neq i}}^{N}e^{-\beta u_{ij}(q_j-q)}=\prod_{\substack{j=1\\ \neq i}}^{N}[1+(e^{-\beta u_{ij}}-1)].$$

Expansion of the continued product gives as a first approximation

$$e^{-\beta u_i(q)}=1+\sum_{\substack{j=1\\ \neq i}}^{N}(e^{-\beta u_{ij}}-1)+\cdots.$$

Now consider an integral of the form

$$\int f(q_j)[e^{-\beta u_{ij}(q)}-1]dv_j.$$

Since $(e^{-\beta u_{ij}(q)}-1)$ is zero except when q_j is in the immediate neighborhood of q, we may write approximately

$$\int f(q_j)[e^{-\beta u_{ij}(q)}-1]dv_j=-2B_{ij}f(q),$$
$$B_{ij}=\tfrac{1}{2}\int(1-e^{-\beta u_{ij}})dv_j.$$

This is a rough but adequate approximation when $f(q_j)$ does not vary rapidly over the small region, in which $u_{ji}(q_j-q)$ is effectively different from zero. It amounts to replacing $f(q_j)$ in this region by its value at the center $q=q_j$. Making this approximation, the function $\zeta_{ki}^{\circ}-1$ becomes with the neglect of terms in C^2,

$$\zeta_{ki}^{\circ}-1=-2\sum_{j}C_jB_{ij}(\zeta_{kj}'-1),$$
$$\zeta_{kj}'=\frac{v\int\cdots\int e^{-\beta[V_{N-2}+V_j(q)]}dv_1\cdots dv_{N-2}}{\int\cdots\int e^{-\beta V_{N-1}}dv_1\cdots dv_{N-1}}.$$

Thus ζ_{kj}' differs from ζ_{kj}, simply by the removal of the single ion i. This removal can produce a change in ζ_{kj} only of the order of ζ_{kj}/N_i, so that effectively $\zeta_{kj}'=\zeta_{kj}$.

$$\overline{{}^{ik}\psi_i(q)} = \overline{{}^{ik}\psi_i(q)}\big|_{e_i=0} + \overline{{}^{ik}\psi_i(q)}\big|_{e_k=0} - \overline{{}^{ik}\psi_i(q)}\big|_{e_i=0;\ e_k=0} + \int_0^{e_i}\int_0^{e_k} \frac{\partial^2 \overline{{}^{ik}\psi_i(q)}}{\partial e_i \partial e_k} de_i de_k. \tag{31}$$

When the charge e_i is zero, we have from Eq. (22)

$$\overline{{}^{ik}\psi_i(q)}\big|_{e_i=0} = \frac{\int\cdots\int \psi_i(q) e^{-\beta[V_{N-1}+u_i(q)]} dv_1\cdots dv_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q)]} dv_1\cdots dv_{N-2}}. \tag{32}$$

Both numerator and denominator of (32) may be multiplied by v, and since both integrands are independent of q_i, all q_i's having been replaced by q, the v factors may be expressed as integrations over the running coordinates q_i.

$$\overline{{}^{ik}\psi_i(q)}\big|_{e_i=0} = \frac{\int\cdots\int \psi_i(q) e^{-\beta[V_{N-1}+u_i(q)]} dv_1\cdots dv_{N-1}}{\int\cdots\int e^{-\beta[V_{N-1}+u_i(q)]} dv_1\cdots dv_{N-1}}. \tag{33}$$

In this expression both q_k and q are of course held fixed during the integrations. With the aid of (2), (27) and (33) we find

$$\overline{{}^{ik}\psi_i(q)}\big|_{e_i=0} = \frac{\overline{{}^{k}\psi_i(q)\zeta_i^{\circ}}\big|_{e_i=0}}{\zeta_{ki}^{c}} = \overline{{}^{k}\psi_i(q)}\big|_{e_i=0} + \frac{\overline{{}^{k}\psi_i(q)\zeta_i^{\circ}}\big|_{e_i=0} - \overline{{}^{k}\psi_i(q)}\big|_{e_i=0}\ \overline{{}^{k}\zeta_i^{\circ}}\big|_{e_i=0}}{\overline{{}^{k}\zeta_i^{\circ}}\big|_{e_i=0}}. \tag{34}$$

The second term in expression (34) depends primarily upon van der Waals forces and is approximately given by

$$\frac{\overline{{}^{k}\psi_i(q)\zeta_i^{\circ}}\big|_{e_i=0} - \overline{{}^{k}\psi_i(q)}\big|_{e_i=0}\ \overline{{}^{k}\zeta_i^{\circ}}\big|_{e_i=0}}{\overline{{}^{k}\zeta_i^{\circ}}\big|_{e_i=0}} = -2\sum_j B_{ij}C_j\zeta_{kj}\left[\frac{3}{2}\frac{e_j}{Da_{ij}} + \overline{{}^{jk}\psi_{ij}(q)}\big|_{e_{i=0}} - \overline{{}^{k}\psi_i(q)}\big|_{e_{i=0}}\right] \tag{35}$$

where the various symbols have the same meaning as in Eq. (29).[9]

Starting from Eq. (24) instead of from (22), we obtain in a similar manner the following expression for $\overline{{}^{ik}\psi_i(q)}\big|_{e_k=0}$

$$\overline{{}^{ik}\psi_i(q)}\big|_{e_k=0} = \overline{{}^{i}\psi_i(q_i)}\big|_{e_k=0} + \frac{\overline{{}^{i}\psi_i(q_i)\zeta_k^{\circ}(q')}\big|_{e_k=0} - \overline{{}^{i}\psi_i(q_i)}\big|_{e_k=0}\ \overline{{}^{i}\zeta_k^{\circ}(q')}\big|_{e_k=0}}{\overline{{}^{i}\zeta_k^{\circ}(q')}\big|_{e_k=0}} \qquad |q'-q_i| = |q-q_k|. \tag{36}$$

As in (34), the second term of (36) is small, and depends primarily upon van der Waals forces.

The potential $\overline{{}^{ik}\psi_i(q)}\big|_{e_i=0;\ e_k=0}$ is of course zero if all ions are of equal size, that is if all u_{ki} have the same form. If the sizes are unequal $\overline{{}^{ik}\psi_i(q)}\big|_{e_i=0,\ e_k=0}$ will consist of a small term proportional to the concentration, arising from a statistical double layer on the surface of the ion i.

Differentiation of Eq. (21) leads to the following expression for $\partial^2\overline{{}^{ik}\psi_i(q)}/\partial e_i\partial e_k$

$$\frac{\partial^2 \overline{{}^{ik}\psi_i(q)}}{\partial e_i \partial e_k} = \beta^2\ \overline{[\psi_k(q_k) - {}^{ik}\psi_k(q_k)][\psi_i(q) - {}^{ik}\psi_i(q)]}^{ik}. \tag{37}$$

This derivative is thus a fluctuation of the third order.

Combining (34), (36) and (37), we obtain, remembering that quantities with the subscript, $e_i=0$, are independent of e_i

$$\int_0^{e_i} [\overline{{}^{ik}\psi_i(q)} - \overline{{}^{k}\psi_i(q_i)}]de_i = e_i \overline{{}^{k}\psi_i(q)}|_{e_i=0} + \int_0^{e_i} [\overline{{}^{i}\psi_i(q_i)}|_{e_k=0} - \overline{{}^{k}\psi_i(q_i)}]de_i + \varphi_{ki}(q), \tag{38}$$

where $\varphi_{ki}(q) = \int_0^{e_i}\int_0^{e_i}\int_0^{e_k} \beta^2 \overline{[\psi_k(q_k) - {}^{ik}\psi_k(q_k)][\psi_i(q) - {}^{ik}\psi_i(q)]^2}de_i de_i de_k$

$$+e_i\left[\frac{\overline{{}^{k}\psi_i(q)\zeta_i^{\circ}(q)}|_{e_i=0} - \overline{{}^{k}\psi_i(q)}|_{e_i=0}\,\overline{{}^{k}\zeta_i^{\circ}(q')}|_{e_i=0}}{\overline{{}^{k}\zeta_i^{\circ}(q)}|_{e_i=0}} - \overline{{}^{ik}\psi_i'(q)}|_{e_i=0,\ e_k=0}\right]$$

$$+\int_0^{e_i}\left[\frac{\overline{{}^{i}\psi_i(q_i)\zeta_k^{\circ}(q')}|_{e_k=0} - \overline{{}^{i}\psi_i(q_i)}|_{e_k=0}\,\overline{{}^{i}\zeta_k^{\circ}(q')}|_{e_k=0}}{\overline{{}^{i}\zeta_k^{\circ}(q')}|_{e_k=0}}\right]de_i. \tag{39}$$

It is readily seen that the mean potential $\overline{{}^{k}\psi_i(q)}|_{e_i=0}$ differs from $\overline{{}^{k}\psi(q)}$ by a quantity of order $\overline{{}^{k}\psi(q)}/N_i$ where N_i is the number of ions of the ith type. In an averaging process in which only the k ion is held fixed, all ions of the ith type are equivalent. Thus the discharge of a single i ion would alter the potential only by a quantity of negligible order $(1/N_i)$. (The discharge of a single ion of course destroys the electrical neutrality of the solution but in a completely trivial manner.) For the same reason $\overline{{}^{i}\psi_i(q_i)}|_{e_k=0}$ can be identified with $\overline{{}^{i}\psi_i(q_i)}$. Since by Eq. (11) this latter potential is equal to $\bar{\psi}_i$, we may identify $\overline{{}^{i}\psi_i(q_i)}|_{e_k=0}$ with ψ_i. Further it is clear that $\overline{{}^{k}\psi_i(q_i)}$ also differs from $\bar{\psi}_i$ by a quantity of negligible order. The fixed ion k can influence the potential and distribution in the neighborhood of a particular ion i, only when that ion is in a region around k, having a volume, ω, of molecular order of magnitude. But the ratio of the probability that an ion i will be in this small volume to the probability that it will be elsewhere in the solution is roughly ω/v, or a quantity of negligible order. Since $\overline{{}^{i}\psi_i(q_i)}|_{e_k=0}$ and $\overline{{}^{k}\psi_i(q_i)}$ are both effectively equal to $\bar{\psi}_i$ the second term of (38) vanishes. Further, since $\overline{{}^{k}\psi_i(q)}|_{e_i=0}$ is effectively equal to $\overline{{}^{k}\psi(q)}$, we may write

$$\int_0^{e_i} [\overline{{}^{ik}\psi_i(q)} - \overline{{}^{k}\psi_i(q_i)}]de_i = e_i \overline{{}^{k}\psi(q)} + \varphi_{ki}(q). \tag{40}$$

This relation is exact to quantities of order $1/N$, where N is the total number of ions. When relation (40) is introduced into Eq. (28), the mean Poisson equation becomes

$$\nabla^2 \overline{{}^{k}\psi(q)} = -\frac{4\pi}{D}\sum_i c_i e_i \zeta_{ki}^{\circ} e^{-\beta[e_i \overline{{}^{k}\psi(q)} + \varphi_{ki}(q)]}. \tag{41}$$

This equation is statistically exact, since only quantities of negligible order of magnitude, $0(1/N)$, have been neglected in its derivation. From now on, we shall begin to make approximations. Suppose we assume the ions to be rigid spheres and neglect van der Waals forces of the attractive type. Let a_k be the mean distance of closest approach of the other ions to ion k. The primary effect of van der Waals forces is to make the ζ_{ki}° vanish inside the sphere a_k. If secondary effects of van der Waals forces in ζ_{ki}° and in φ_{ki} are ignored, Eq. (41) becomes:[10]

[10] The simplification of (41) when the ions are assumed to have different sizes is more elaborate, but offers no difficulty. Except for the fluctuation terms, the equations are identical with those employed by Scatchard in the treatment of this case. (G. Scatchard, Phys. Zeits. **33**, 22 (1932).)

$$\nabla^2 \overline{{}^{k}\psi(q)} = -\frac{4\pi}{D}\sum_i c_i e_i e^{-\beta[e_i \overline{{}^{k}\psi(q)} + \varphi_{ki}(q)]}; \qquad |\mathbf{r}-\mathbf{r}_k| > a_k$$
$$= 0; \qquad |\mathbf{r}-\mathbf{r}_k| \leq a_k; \tag{42}$$
$$\varphi_{ki}(q) = \beta^2 \int_0^{e_i}\int_0^{e_i}\int_0^{e_k} \overline{{}^{ik}[\psi_k(q_k) - \overline{{}^{ik}\psi_k(q_k)}][\psi_i(q) - \overline{{}^{ik}\psi_i(q)}]^2}\, de_i de_i de_k.$$

If the fluctuation terms φ_{ki} are neglected, Eq. (42) reduces to the fundamental equation of the Debye-Hückel theory.

$$\nabla^2 \overline{{}^{k}\psi(q)} = -\frac{4\pi}{D}\sum_i e_i c_i e^{-\beta e_i \overline{{}^{k}\psi(q)}}; \qquad |\mathbf{r}-\mathbf{r}_k| > a_k \tag{43}$$
$$= 0; \qquad |\mathbf{r}-\mathbf{r}_k| \leq a_k.$$

The nature of this approximation becomes clearer when the fluctuation (37) is expressed in terms of $\overline{{}^{ik}\psi_k(q_k)}$, the mean potential in the ion k, when the ion i is held fixed at the point q. We recall that

$$\overline{{}^{ik}\psi_k(q_k)} = \frac{\int\cdots\int \psi_k(q_k) e^{-\beta[V_{N-1}+V_i(q)]} dv_1 \cdots dv_{N-2}}{\int\cdots\int e^{-\beta[V_{N-1}+V_i(q)]} dv_1 \cdots dv_{N-2}}. \tag{44}$$

By differentiation of (44), we find

$$\overline{{}^{ik}[\psi_k(q_k) - \overline{{}^{ik}\psi_k(q_k)}][\psi_i(q) - \overline{{}^{ik}\psi_i(q)}]^2} = \frac{1}{\beta^2}\frac{\partial^2 \overline{{}^{ik}\psi_k(q_k)}}{\partial e_i^2}. \tag{45}$$

Suppose that $\overline{{}^{ik}\psi_k(q_k)}$ is expanded in a Taylor's series of the form

$$\overline{{}^{k}\psi_k(q_k)} = \overline{{}^{ik}\psi_k(q_k)}\big|_{e_i=0} + e_i\left[\frac{\partial \overline{{}^{ik}\psi_k(q_k)}}{\partial e_i}\right]_{e_i=0} + \sum_{n=2}^{\infty}\frac{e_i^n}{n!}\left[\frac{\partial^n \overline{{}^{ik}\psi_k(q_k)}}{\partial e_i^n}\right]_{e_i=0}. \tag{46}$$

If it is a sufficient approximation to neglect all but the first two terms of the expansion (46), the fluctuation (45) and also the integrated fluctuation φ_{ki} vanish. Thus, we see that the neglect of the fluctuation terms is equivalent to assuming that $\overline{{}^{ik}\psi_k(q_k)}$ can be approximated by a linear function of the charge, e_i, on the ion i. When the point q, at which the ion i is situated, is at a large distance from the ion k, we should expect this to be a rather good approximation. Moreover, aside from the neglect of certain secondary effects of van der Waals forces, it is the only approximation involved in the derivation of the Debye-Hückel Eq. (43) from statistical mechanics. This is a rather striking fact, for the opinion was generally held that the neglect of the local influence of the ion i, when situated at q, on the potential and distribution in the neighborhood of the ion k, was only one of the defects of the Debye theory. However, it appears that not even this factor is entirely neglected.

It is interesting to remark that φ_{ki} depends entirely upon the screening influence of the statistical space charge on the interaction of the ions i and k, and therefore vanishes at zero ionic concentration. Thus we may write

$$\lim_{c=0} \overline{{}^{ik}\psi_k(q_k)} = \frac{e_i}{Dr}; \quad r = |\mathbf{r}-\mathbf{r}_k|$$
$$\lim_{c=0} \frac{\partial^2 \overline{{}^{ik}\psi_k(q_k)}}{\partial e_i^2} = 0 \tag{47}$$

and therefore by Eqs. (42) and (45)

$$\lim_{c=0} \varphi_{ki} = 0. \tag{48}$$

The potential $\overline{{}^{k}\psi(q)}$, on the other hand, approaches e_k/Dr, so that

$$\lim_{c=0} \varphi_{ki}(q) \Big/ \overline{{}^{k}\psi(q)} = 0. \tag{49}$$

Eq. (49) suggests that we might use solutions of the Debye-Hückel Eq. (43) to obtain a first approximation to $\overline{{}^{ik}\psi_k(q_k)}$, which we require to

obtain an estimate of φ_{ki}. When the distance $|\mathbf{r}-\mathbf{r}_k|$ between the fixed ions i and k is large, we should expect to obtain a fair approximation to $\overline{{}^{ik}\psi_k(q_k)}$ by writing

$$\overline{{}^{ik}\psi_k(q_k)} = \overline{{}^{k}\psi_k(q_k)} + \overline{{}^{i}\psi(q_k)}\big|_{q_i=q}. \tag{50}$$

This approximation involves the assumption that the statistical space charges around the ions i and k are additive, in other words that they overlap without mutual interference. More exactly, it can be shown to be equivalent to neglecting a fourth order fluctuation of the form

$$\overline{[\psi_k(q_k) - {}^{ik}\psi_k(q_k)]^2[\psi_i(q) - {}^{ik}\psi_i(q)]^2}$$

in the derivative, $\partial^2\,\overline{{}^{ik}\psi_k(q_k)}/\partial e_2^2$.

In this approximation, we have, since the derivatives of $\overline{{}^{k}\psi_k(q_k)}$ with respect to e_i are of negligible magnitude $0(1/N_i)$

$$\frac{\partial^2\,\overline{{}^{ik}\psi_k(q_k)}}{\partial e_i^2} = \frac{\partial^2\,\overline{{}^{i}\psi(q_k)}\big|_{q_i=q}}{\partial e_i^2}. \tag{51}$$

Now $\overline{{}^{i}\psi(q_k)}\big|_{q_i=q}$, equal to $\overline{{}^{i}\psi(|\mathbf{r}-\mathbf{r}_k|)}$, satisfies an equation of the type (42). Let us try as an approximation, the Gronwall-La Mer-Sandved[11] solution of the Debye-Hückel Eq. (43).

$$\overline{{}^{i}\psi(q_k)}\big|_{q_i=q} = \sum_{m=1}^{\infty}(-\beta)^{m-1}\left(\frac{e_i}{Da_i}\right)^m \psi_m(a_i, r), \quad r=|\mathbf{r}-\mathbf{r}_k|, \tag{52}$$

where the ψ_m (in the Gronwall-La Mer notation $\epsilon^{m-1}\psi_m$) are symmetrical functions of the ionic charges, $e_1\cdots e_N$: and their derivatives with respect to the charge e_j of any single ion are quantities of negligible order of magnitude. From Eqs. (42), (45), (51) and (52), we obtain the following estimate of the integrated fluctuation φ_{ki}.

$$\varphi_{ki}(r) = e_k\sum_{m=2}^{\infty}(-\beta)^{m-1}\left(\frac{e_i}{Da_i}\right)^m \psi_m(a_i, r). \tag{53}$$

No claim is made that this estimate is exact, but it probably is of the right order of magnitude. We see that it does not involve the initial Debye approximation ($m=1$) at all, but only the Gronwall-La Mer correction terms $m\geqq 2$. Since the $\varphi_{ki}(r)$ of Eq. (53) are not exact, it would not be worth while to employ them in the tedious integration of Eq. (42). However, without detailed calculation, it is easily seen that they cannot influence the initial Debye approximation to $\overline{{}^{k}\psi(q)}$, although they may make contributions comparable with, but probably somewhat smaller than the Gronwall-La Mer correction terms. We should expect their contributions to be small under the same conditions that the Gronwall-La Mer terms are small, namely when

$$e_ke_i/DrkT \ll 1 \text{ for all } e_i. \tag{54}$$

At distances from the ion k, such that the above condition (54) is satisfied, the initial Debye approximations to $\overline{{}^{k}\psi(q)}$ and to $\overline{{}^{k}\rho(q)}$ should be adequate and the Poisson Eq. (42) should reduce effectively to the linear equation of the Debye-Hückel theory.

$$\left.\begin{aligned} &\nabla^2\,\overline{{}^{k}\psi(q)} - \kappa^2\,\overline{{}^{k}\psi(q)} = 0, \quad \kappa^2 = \frac{4\pi}{DkT}\sum_i c_ie_i^2, \\ &r>r_0; \quad \frac{e_ke_i}{Dr_0kT_i} \ll 1. \end{aligned}\right\} \tag{55}$$

If it happens that the ions are so large that the following condition is fulfilled

$$e_ke_i/Da_kkT \ll 1 \text{ for all } e_i. \tag{56}$$

Eq. (55) would be a good approximation in the entire region outside the boundary sphere a_k, as assumed in the original formulation of the Debye-Hückel theory. These statements cannot be regarded as rigorously established without an exact calculation of the fluctuation terms, but the present estimate of the φ_{ki} seems reliable enough to make them convincing.

The exact determination of the fluctuation terms, φ_{ki} is very difficult, and no convenient means of calculation has yet been devised. However, it seems worth while to outline a possible method of successive approximation. If the mean potential $\overline{{}^{ik}\psi_k(q_k)}$ is known, φ_{ki} may be calculated from its second derivative with respect to e_i. Now

$$\overline{{}^{ik}\psi_k(q_k)} = \overline{{}^{ik}\psi_k(q_k; q, q_k)}, \tag{57}$$

[11] Gronwall, La Mer and Sandved, Phys. Zeits. **29**, 358 (1928).

where $^{ik}\overline{\psi(q_k;\ q,\ q_k)}$ is the value of the mean potential $^{ik}\overline{\psi(q';\ q_i,\ q_k)}$ given by Eq. (22) when $q'=q_k$ and $q_i=q$. By the same methods employed in the derivation of Eq. (28), it may be shown that $^{ik}\overline{\psi(q',\ q_i,\ q_k)}$ satisfies the following Poisson equation:

$$(\nabla')^2\,{}^{ik}\overline{\psi(q';\ q_i,\ q_k)}=$$
$$-\frac{4\pi}{D}\sum_i c_j e_j \zeta^\circ{}_{ikj}\times e^{-\beta\int_0^{e_j}{}^{ijk}\overline{[\psi_j(q')-\ {}^{ik}\overline{\psi_j(q_j)}]}\,de_j}. \qquad (58)$$

The exact solution of this equation would require the knowledge of fluctuation terms depending on a mean potential $^{ijk}\overline{\psi}$, which may be shown to satisfy a Poisson equation similar to (58). By setting up a series of Poisson equations for $^{1}\overline{\psi}$, $^{2}\overline{\psi}$, $\cdots$ $^{n}\overline{\psi}$ in which 1, 2, $\cdots$ n ions are, respectively, held fixed during the averaging process, and neglecting fluctuation terms in the equation for $^{n}\overline{\psi}$, one could presumably obtain any desired degree of approximation by making n large enough. To obtain an exact solution, one would have to set up a system of Poisson equations for $N-1$ mean potentials, $^{1}\psi$, $\cdots$ $^{N-1}\overline{\psi}$ and solve them simultaneously. However, when n becomes of the same order of magnitude as N, one can no longer make the simplifications in the statistical charge density that are possible for small n, and one has a set of simultaneous integro-differential equations, which are virtually impossible to solve.

The solution of Eq. (58) for $^{ik}\overline{\psi(q';\ q_i,\ q_k)}$ is difficult, even in the Debye-Hückel approximation corresponding to (43), since two ionic centers are involved. A solution of this equation in the initial Debye approximation corresponding to Eq. (55) has been obtained by Scatchard and Kirkwood.[12] Using their approximation to $^{ik}\overline{\psi_k(q_k)}$, we find that φ_{ki} vanishes. A solution of the complete Debye-Hückel equation for two ionic centers by the Gronwall-La Mer method has never been carried out, but it is quite certain that it would lead to a value of φ_{ki} of the same form and magnitude as Eq. (53).

It may be objected that, since we have based our calculation of the φ_{ki} upon solutions of a Poisson equation in which similar fluctuation terms were neglected, we have not definitely shown that they cannot be large. The final answer to this question must await an exact calculation of the φ_{ki} by some independent method. We have shown, however, that the Debye-Hückel Eq. (42) is statistically consistent with values of the fluctuation terms of the magnitude of the Gronwall-La Mer terms, and we believe to have presented convincing, if not conclusive evidence that they cannot influence the initial Debye approximation.

IV.

The significance of the Gronwall-La Mer terms remains somewhat ambiguous, due to the fact that the fluctuation terms may make contributions to $^{k}\overline{\psi(q)}$ of comparable although somewhat smaller magnitude. Moreover, even if the φ_{ki} were known with exactness, the integration of Eq. (42) would be complicated and tedious. It therefore seems very desirable to employ the method of Bjerrum[13] or one similar to it in the treatment of ions of small size and high valence, for which the initial Debye approximation is inadequate. The essential feature of Bjerrum's method consists in neglecting the screening effect of other ions on the interaction of an ion pair, k and i, when the two ions are close together. Bjerrum also makes use of a special hypothesis concerning ionic association, which, though intuitively attractive, is in some respects arbitrary. We shall outline an alternative treatment here, which utilizes Bjerrum's screening approximation, but not his association hypothesis. The method leads to a result which is almost identical with that of Bjerrum at low ionic strengths, but which is somewhat different at higher ionic strengths. Although Bjerrum's special hypothesis concerning association is not employed, ionic association in the classical sense involving a continuum of molecular species without sharply graded dissociation energies, is still implicitly taken into account. The method is proposed as an alternative and not necessarily as a substitute for Bjerrum's treatment, for the latter may give better results under conditions favoring a sharply graded binary association of the ions.

The potential $^{k}\overline{\psi_k(r)}$ at a distance r from the

[12] Scatchard and Kirkwood, Phys. Zeits. **33**, 297 (1932).

[13] N. Bjerrum, Kgl. Dan. Vid. Sels. VII, 9 (1926).

ion k, can be expressed in terms of the spherically symmetric charge density, $^k\overline{\rho(r)}$, in the following manner

$$^k\overline{\psi_k(r)}=\frac{4\pi}{Dr}\int_0^r \xi^2\,{}^k\overline{\rho(\xi)}d\xi+\frac{4\pi}{D}\int_r^\infty \xi\,{}^k\overline{\rho(\xi)}d\xi. \quad (59)$$

Because of the van der Waals forces of the repulsive type, $^k\overline{\rho(\xi)}$ vanishes in the neighborhood of $\xi=0$, so that the above expression converges. The value of the potential at the center of the ion k is therefore

$$^k\overline{\psi_k}=\frac{4\pi}{D}\int_0^\infty \xi\,{}^k\overline{\rho(\xi)}d\xi. \quad (60)$$

Further, $^k\overline{\rho(\xi)}$ must satisfy the following normalization condition

$$4\pi\int^\infty \xi^2\,{}^k\overline{\rho(\xi)}d\xi=-e_k. \quad (61)$$

This condition is imposed by the electrical neutrality of the solution as a whole. That it is satisfied by the exact charge density, $^k\overline{\rho(q)}$ of Eq. (14) is easily verified by direct integration of the ζ_{ki}. When the ions are treated as rigid spheres of diameter a, the charge density $^k\overline{\rho(\xi)}$ vanishes when $\xi\leq a$. In this case, the boundary conditions, requiring $^k\overline{\psi(q)}$ and the normal component of its gradient to be equal on the two sides of the boundary sphere a, are automatically fulfilled, when Eqs. (60) and (61) are satisfied. However, these equations are more general than the simple boundary conditions, for they hold even when the ions do not have sharp boundaries.

Let us suppose that r_0 is some distance, beyond which condition (54) is satisfied. Outside of the sphere r_0, the Debye linear equation may be employed to obtain $^k\overline{\psi(r)}$ and $^k\overline{\rho(r)}$

$$\left.\begin{aligned}&\nabla^2\,{}^k\overline{\psi(r)}-\kappa^2\,{}^k\overline{\psi(r)}=0,\\ &{}^k\overline{\psi(r)}=A\frac{e^{-\kappa r}}{r},\\ &{}^k\overline{\rho(r)}=-\frac{D\kappa^2 A}{4\pi}\frac{e^{-\kappa r}}{r},\end{aligned}\right\} r>r_0, \quad (62)$$

where the solution, $e^{+\kappa r}/r$ is excluded since it would make $^k\overline{\psi(r)}$ infinite as r tends to infinity, a physically impossible situation. With the aid of Eqs. (62) and (14), the relations (60) and (61) become

$$\left.\begin{aligned}&{}^k\overline{\psi_k}=\frac{1}{D}\sum_i c_i e_i K_{ki}-\kappa A e^{-\kappa r_0},\\ &-e_k=\sum_i c_i e_i G_{ki}-DA(1+\kappa r_0)e^{-\kappa r_0},\\ &K_{ki}=4\pi\int_0^{r_0}\xi\zeta_{ki}(\xi)d\xi,\\ &G_{ki}=4\pi\int_0^{r_0}\xi^2\zeta_{ki}(\xi)d\xi.\end{aligned}\right\} \quad (63)$$

Eliminating A from these two equations, and making use of Eq. (11), we obtain[14]

$$\bar{\psi}_k=-\frac{1}{D}[e_k+\sum_i c_i e_i G_{ki}]\frac{\kappa}{1+\kappa r_0}+\frac{1}{D}\sum_i c_i e_i K_{ki}. \quad (64)$$

At small concentrations the ζ_{ki} become independent of the ionic strength, and the above expression approaches the limiting law of the Debye-Hückel theory. If the mean diameter of the ions is such that condition (55) is fulfilled, we may take $r_0=a_k$, and the integrals G_{ki} and K_{ki} vanish. We are then left with the initial Debye approximation to $\bar{\psi}_k$. When (55) is not satisfied, we may obtain approximate expressions for the integrals K_{ki} and G_{ki} by neglecting the influence of screening on the functions ζ_{ki} when r is less than r_0. When screening is neglected, we may write

$$\left.\begin{aligned}&{}^k\overline{\psi(r)}=e_k/Dr;\quad {}^{ik}\overline{\psi_k(q_k)}=e_i/Dr;\\ &\partial^2\,{}^{ik}\overline{\psi_k(q_k)}/\partial e_i{}^2=0;\quad r\leq r_0.\end{aligned}\right\} \quad (65)$$

Thus the neglect of screening causes the fluctuation (45) to vanish, and we have

$$\varphi_{ki}(r)=0;\quad r\leq r_0. \quad (66)$$

For simplicity, we assume that the molecules are rigid spheres and neglect attractive van der Waals forces. If we denote the mean diameter of the ion k and an ion of the type i by a_{ki}, and remember that ζ_{ki} must vanish when $r\leq a_{ki}$, we may write

$$\left.\begin{aligned}\zeta_{ki}&=e^{-\beta e_i e_k/Dr};\quad a_{ki}<r\leq r_0\\ &=0;\quad r\leq a_{ki}\end{aligned}\right\} \quad (67)$$

[14] It should be remarked that $\Sigma_i e_i c_i G_{ki}$ and $\Sigma_i e_i c_i K_{ki}$ are opposite in sign to e_k, since the intergals G_{ki} and K_{ki} are much greater when e_i is opposite in sign to e_k than when of the same sign.

and the integrals K_{ki} and G_{ki} become

$$K_{ki}=4\pi\int_{a_{ki}}^{r_0}\xi e^{-\beta e_i e_k/D\xi}d\xi,$$
$$G_{ki}=4\pi\int_{a_{ki}}^{r_0}\xi^2 e^{-\beta e_i e_k/D\xi}d\xi. \tag{68}$$

Except for the fact that condition (54) must be satisfied, the distance r_0, within which screening is neglected, is somewhat arbitrary. It may be chosen in the manner which Bjerrum proposes, or perhaps by some more convenient criterion. As in Bjerrum's theory, the integrals K_{ki} and G_{ki} are fortunately very insensitive to its value. However, we must certainly require that r_0 be less than $1/\kappa$, for the neglect of screening to a distance comparable with $1/\kappa$ would be a rather drastic approximation.

When screening is neglected in the calculation of K_{ki} and G_{ki}, the approximate $\bar{\psi}_k$ no longer satisfies the condition of integrability (4). However, if r_0 is treated as independent of the ionic charges, the integrability condition is satisfied up to terms in κ^3. Bjerrum circumvents this difficulty by means of his association hypothesis, but does not overcome it. In fact it would be somewhat fortuitous if any approximate $\bar{\psi}_k$ exactly satisfied the integrability condition, unless the method of approximation was specifically chosen with that purpose in mind.

Approximate expressions for the logarithm of the activity coefficient of the ion k may be obtained from Eqs. (64) and (68) with the aid of either the Debye or the Güntelberg-Müller charging process. They differ very little from the corresponding expressions of Bjerrum at low ionic strength. We hope to develop the method more fully at a later time, choosing, if possible, better approximations to the integrals K_{ki} and G_{ki}, which are consistent with the condition of integrability.

We recall that Bjerrum's treatment leads to numerical values of activity coefficients, which differ very little from those obtained from the Gronwall-La Mer-Sandved potential, when the latter converges sufficiently rapidly. Since Eq. (64) leads to essentially the same result as the Bjerrum method, when screening is neglected, we have indirect evidence that the Gronwall-La Mer-Sandved potential is probably a fairly good approximation in spite of the neglect of fluctuation terms. In other words, the neglect of all screening effects at small distances, of which the fluctuation terms are a part, leads to a result which differs but little from that of Gronwall and La Mer, who neglected only fluctuation terms. This suggests the conclusion that all screening effects, including fluctuations, are unimportant at small distances, in comparison with the large constant term e_k/Dr in both the mean potential and the potential of the mean force.

V.

It seems worth while to discuss briefly the relation of the general theory of fluctuations to the properties of electrolyte solutions, since it has occasionally been the source of some misunderstanding. Suppose that Y is some additive property of a macroscopic system consisting of N microscopic systems, for example molecules or ions. If y_k is the contribution of the microscopic system k to Y, we may write

$$Y=\sum_{k=1}^{N}y_k, \quad \bar{Y}=\sum_{k=1}^{N}\bar{y}_k, \tag{69}$$

since the averaging process is a linear operation. The same equality does not hold for the mean square fluctuations $\overline{(Y-\bar{Y})^2}$ and $\sum_{k=1}^{N}\overline{(y_k-\bar{y}_k)^2}$, which in general are not only unequal but of entirely different orders of magnitude. We say that Y is a normal property of the macroscopic system (sensibly constant to external observation, with the value $\bar{Y}$) when $\overline{(Y-\bar{Y})^2}$ is very small relative to $\bar{Y}^2$. This in no way implies that $\overline{(y_k-\bar{y}_k)^2}$ must be small relative to $\bar{y}_k^2$. In general, this is not the case, nor would we expect it to be, for a single molecule or a small number of molecules does not have normal properties in the thermodynamic sense. However, the fact that $\overline{(y_k-\bar{y}_k)^2}$ may be of the same or greater magnitude as $\bar{y}_k^2$, in no way invalidates Eq. (69). $\bar{Y}$ is still the sum of the $\bar{y}_k$, and Y is a normal property if $\overline{(Y-\bar{Y})^2}/\bar{Y}^2$ is small. In fact, unless $\overline{(y_k-\bar{y}_k)^2}$ happens to be specifically employed in the calculation of $\bar{y}_k$, its value is quite irrelevant.

Let us consider the mean electrostatic energy of the solution[15]

$$\overline{W}=\sum_{k=1}^{N}\overline{w}_k;\quad \overline{w}_k=\tfrac{1}{2}e_k\overline{\psi}_k. \tag{70}$$

We may write at once

$$\overline{(w_k-\overline{w}_k)^2}/\overline{w}_k^2=\overline{(\psi_k-\overline{\psi}_k)^2}/\overline{\psi}_k^2, \tag{71}$$

where $\overline{(\psi_k-\overline{\psi}_k)^2}$, which has been calculated by Halpern,[5] is given by

$$\overline{(\psi_k-\overline{\psi}_k)^2}=-kT\partial\overline{\psi}_k/\partial e_k. \tag{72}$$

If the $\overline{\psi}_k$ is assumed, as a first approximation, to be linear in e_k, as for example in the Debye limiting law, we have from relations (71) and (72)

$$\overline{(w_k-\overline{w}_k)^2}/\overline{w}_k^2=-kT/e_k\overline{\psi}_k. \tag{73}$$

In dilute solutions, $-kT/e_k\overline{\psi}_k$ as estimated from experimental values of the activity coefficient, or from the Debye limiting law, is in general much greater than unity, so that $\overline{(w_k-\overline{w}_k)^2}$ is usually greater than $\overline{w}_k^2$. This fact alone in no way invalidates the Debye limiting law. It should be remarked that if the magnitude of $\overline{(w_k-\overline{w}_k)^2}/\overline{w}_k^2$ were taken as a criterion for the validity of statistical calculations of the type of Eq. (69), it would invalidate not only the Debye limiting law but also any other limiting law. In fact by a similar line of reasoning one could cast doubt upon the ideal gas law, $pv=NkT$, since the fluctuation $\overline{(\epsilon-\bar{\epsilon})^2}$ in the energy of a single gas molecule is equal to $\frac{2}{3}\bar{\epsilon}^2$ where $\bar{\epsilon}$ is the mean energy of a single molecule. Of course, the fluctuation in the total energy of an ideal gas, consisting of N molecules is such that $\overline{(E-\overline{E})^2}/\overline{E}^2=2/(3N)$, or negligible if N is large, let us say of the order of 10^{20}.

It is easily shown that, while $\overline{(w_k-\overline{w}_k)^2}/\overline{w}_k^2$ may be large, $\overline{(W-\overline{W})^2}/\overline{W}^2$ is always negligibly small in solutions of finite volume and finite concentration, amenable to thermodynamic measurement. Thus, it is easily demonstrated that

$$\overline{(W-\overline{W})^2}=-\frac{kT}{2}\left\{\frac{\partial}{\partial\lambda}\left[\frac{\overline{W}(\lambda e_1\cdots\lambda e_N)}{\lambda^2}\right]\right\}_{\lambda=1}. \tag{74}$$

If the mean electrostatic energy $\overline{W}$ is assumed to be a homogeneous function of degree three in the ionic charges, $e_1\cdots e_N$, as for example, according to the Debye-Hückel limiting law

$$\frac{\overline{W}(\lambda e_1\cdots\lambda e_N)}{\lambda^2}=\lambda\overline{W},$$

$$\frac{\overline{(W-\overline{W})^2}}{\overline{W}^2}=-\frac{1}{2}\frac{kT}{\overline{W}}\sim\frac{1}{N}\left(\frac{1}{2}\frac{kT}{e_k\overline{\psi}_k}\right). \tag{75}$$

Now $-kT/2e_k\psi_k$ is of the order of magnitude of $(-\log\gamma_\pm)^{-1}$, where $\gamma_\pm$ is the mean activity coefficient of the ions. Moreover, in all solutions of thermodynamic interest $(-N\log\gamma_\pm)^{-1}$ is a very small quantity, of an order of magnitude not greater than about 10^{-10} in all solutions of sufficient volume and concentration to be of thermodynamic interest. Thus W is certainly a normal property of electrolyte solutions. Of course, strictly speaking, it ceases to be such at zero electrolyte concentration, but long before mathematically zero concentration is reached both $\overline{W}$ and $\overline{(W-\overline{W})^2}$ become too small for thermodynamic observation.

If it were true that a quadratic fluctuation of the type $\overline{(\psi_k-\overline{\psi}_k)^2}$ had been neglected in the Poisson-Boltzmann equation, there would be an adequate basis for objecting to the Debye limiting law since $\overline{(\psi_k-\overline{\psi}_k)^2}$ is of the order of κ. It is to be emphasized, however, that no such quadratic fluctuation is neglected, but only the difference between the mean potential and the potential of the mean force. We have shown that this difference may be expressed in terms of a third order fluctuation of the potential, which does not affect the initial Debye approximation to the mean potential and is small at large distances from the central ion. Further, this fluctuation term depends entirely upon the screening action of the statistical space charge and therefore its influence on the distribution function at small distances from the central ion is small compared with that of the Coulomb term, e_k/Dr, at low ionic concentrations.

[15] W is related to the thermodynamic energy of the solution in the following manner:

$$E-E_0=\overline{W}[1+(\partial\log D/\partial\log T)_v]$$

where E is the energy when all ions are fully charged and E_0 is the energy when they are completely discharged.

A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities

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A new approximate "absolute" scale of electronegativity, or electroaffinity, is set up. The absolute electroaffinity on this scale is equal to the average of ionization potential and electron affinity. These quantities must, however, in general, be calculated not in the ordinary way, but for suitable "valence states" of the positive and negative ion. Also, the electroaffinity of an atom has different values for different values of its valence; in general the electroaffinity as here calculated (in agreement with chemical facts) is larger for higher valences. Electroaffinity values have been calculated here for H, Li, B, C, N, O, F, Cl, Br, I. They show good agreement in known cases with Pauling's electronegativity scale based on thermal data, and with the dipole moment scale. The present electronegativity scale (like the others) is rather largely empirical, especially as to its quantitative validity; and it remains to be seen whether or not the latter will be more than very rough when tested for a wider range of cases. Nevertheless the new scale has a degree of theoretical background and foundation which throws some new light on the physical meaning of the concept of electronegativity (or electroaffinity). The basis of the present scale, it should be mentioned, is simpler and more certain for univalent than for polyvalent atoms.—The nature of valence states of atoms is briefly discussed. It is hoped that the tabulations of atomic valence state energies and valence state ionization potentials and electron affinities given at the end of this paper may be useful in problems of molecular structure.

A. UNIVALENT ATOMS

ONE of the most familiar and useful of chemical concepts is that of relative electronegativity. The physical basis of this has remained obscure, although it has been evident that the electronegativity of an atom must be related somehow to its electron affinity or its ionization potential, or both. Recently two empirical scales of relative electronegativity have been set up. In the present paper, a possible third, absolute, scale is discussed.

In general, the wave function of a molecule AB, where A and B are both univalent, can be approximated by forming a linear combination of a wave function, which may be symbolized by $\psi(A-B)$, corresponding to a state with a Pauling-Slater electron-pair bond, with two wave functions corresponding to ionic states A^+B^- and A^-B^+. That is, approximately,[1, 2]

$$\psi_{AB}=\gamma\psi(A-B)+\alpha\psi(A^+B^-)+\beta\psi(A^-B^+). \quad (1)$$

If $\alpha=\beta$, we have a bond which, although it contains polar terms, is almost as purely nonpolar as any bond can be, and is a typical covalent bond.[2] If A and B are identical, $\alpha=\beta$ is obviously necessary; here γ is much larger than α or β.[1] For A not identical with B, Pauling states[2] that "if the two atoms have the same degree of electronegativity," then "the terms corresponding to A^+B^- and A^-B^+ will occur with the same coefficient"; that is, $\alpha=\beta$. For a highly polar molecule with A positive, α exceeds γ and β.

Starting with the above idea, Pauling has succeeded in setting up an empirical scale of approximate relative electronegativities on the basis of thermal data interpreted with the help of a simple quantum-mechanical argument.[2] The consistency of observed thermal data with relations demanded by the scale is rather good, indicating that a fairly definite electronegativity value can be assigned to each element, as one would indeed expect from general chemical experience. In connection with these and other electronegativity values, however, it should be borne in mind that we do not know electronegativity to be a concept capable of exact quantitative definition.

We may now inquire whether there is any way of determining theoretically the conditions under which $\alpha=\beta$ is to be expected in Eq. (1), other than when $A\equiv B$. Let us suppose we have a case where the energy required to produce A^++B^- from A+B is the same as that required to produce A^-+B^+. Further, let us imagine that A^+ and B^- approach each other without deformation, until the distance between their nuclei is equal to the value r_e which occurs in the actual molecule AB; and the same for A^- and B^+. If the

[1] Cf. J. C. Slater, Phys. Rev. **35**, 514–5 (1930) for the case of H_2. Also S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

[2] Cf. L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

energy given out should be the same in the two cases, then the net energy of the two imagined forms A^+B^- and A^-B^+ would be the same, for $r=r_e$ (and nearly, if not exactly, so for other values of r). Then in the actual molecule, according to quantum mechanics, both should participate equally, i.e., $\alpha=\beta$ in Eq. (1), provided (see later paper in this journal)

$$\int \psi(A-B)H\psi(A^+B^-)d\tau - E\int \psi(A-B)\psi(A^+B^-)d\tau = \int \psi(A-B)H\psi(A^-B^+)d\tau - E\int \psi(A-B)\psi(A^-B^+)d\tau,$$

a condition whose approximate fulfillment, for two atoms A and B of equal electronegativity, seems plausible (E=actual energy of ψ_{AB}).

Actually, we cannot expect the conditions mentioned, in particular that of equal energy of attraction of A^++B^- and A^-+B^+, to be met exactly. The equal energy condition would, of course, always be fulfilled if only the simple inverse-square attraction of opposite charges were involved. To this is added, however, a balancing repulsive force which may in general be expected to differ in the two cases. No simple means of estimating the magnitudes of such differences is evident, although crystal lattice data would have some bearing. These are, however, not available for the particular combinations A^+B^- and A^-B^+ in which we are mainly interested.

Let us, nevertheless, as a trial assumption to be tested empirically, suppose that this difference between A^+B^- and A^-B^+ can be neglected, and that the other condition mentioned above is fulfilled. Then whenever we have

$$I_A-E_B=I_B-E_A, \tag{2}$$

we expect $\alpha=\beta$ in Eq. (1), so that A and B are of equal electronegativity according to Pauling's definition. Here I and E stand for ionization potential and electron affinity, respectively; both may conveniently be expressed in volts. If (2) holds, then

$$I_A+E_A=I_B+E_B. \tag{3}$$

[That the equality of the quantities $(I+E)/2$ for two atoms is an approximate criterion for their equal participation in a chemical bond has already been stated by Hund,[3] presumably on the basis of an argument like that just given, although Hund does not go through this, nor refer to the concept of electronegativity: cf. subsequent paper in later issue for further details.] According to Eq. (3), two univalent atoms have equal electronegativity if the sum—or average—of ionization potential plus electron affinity is the same for each.

This suggests that we may define the absolute electronegativity of an atom A approximately as I_A+E_A or, probably better for some purposes, as $(I_A+E_A)/2$. Note that I_A and E_A are really the ionization potentials of A and A^-, respectively. The suggested definition carries with it the implication that the electronegativity of an atom is approximately independent of its closeness of approach to another atom. For our definition is based on the assumption that the net total energy, at $r=r_e$ of AB, is nearly the same for A^++B^- as for A^-+B^+; it is of course, certain that this equality holds for large values of r (Coulomb forces only).

Referring back to Eq. (1), one can readily see qualitatively why E_A and I_A are of equal importance for the electronegativity of an atom A. The negativeness of atom A in ψ_{AB} is greater the larger the coefficient β and the smaller the coefficient α. (For atom B the relations are reversed.) Coefficient β is large if $\psi(A^-B^+)$ is of low energy, and this is favored by large E_A. Coefficient α is small if $\psi(A^+B^-)$ is of high energy, and this is favored by large I_A. One sees then that large E_A and large I_A both help to promote negativeness of atom A in AB. The fact that precisely the quantity $(E_A+I_A)/2$ is a good measure of electronegativity is less obvious, but will be shown *empirically* in the following, by comparison of an $(E_A+I_A)/2$ scale with other empirically established scales of electronegativity. In a subsequent paper, the theoretical basis of the various electronegativity scales will be gone into more thoroughly.

The foregoing discussion indicates the necessity of considering both the $\psi(A^+B^-)$ and the

[3] F. Hund, Zeits. f. Physik **73**, 1 (1931); cf. especially pp. 18–19.

TABLE I. *Electroaffinities.*

Atom and state (*a*)	Electroaff. Abs. electroaff. (*b*)	Electroaff. rel. to H($b-7.12$) (*c*)	(c) ÷2.70 (*d*)	Thermal (*e*)	Elec. Mom. ×10¹⁸ (*f*)
H(s, V_1)	7.12	0.00	0.00	0.00	0.00
F(p^5, V_1)	12.66±0.2	5.54	2.05	2.00	—
Cl(p^5, V_1)	9.81±0.2	2.69	1.00	0.94	1.03
Br(p^5, V_1)	9.06±0.2	1.94	0.72	0.75	0.78
I(p^5, V_1)	8.23±0.3	1.11	0.41	0.40	0.38
O(p^4, V_2)	10.02±0.5 11.4 ±1:II	2.90 4.3	1.07 1.6	1.40	1.53 (104° angle in H_2O)
N(s^2p^3, V_3)	7.40±0.4	0.28	0.10	0.95	1.04 (if 100° angle in NH_3)
	[8.9?] :II	[1.8?]	[0.66?]		
(sp^4, V_3)	8.50±0.4	1.38	0.51		
	20.76±0.7s	13.64	5.05		
	12.58±0.5q	5.46	2.02		
C(s^2p^2, V_2)	5.38±0.3	−1.74	−0.64	[−0.28] p	
(sp^3, V_4)	5.93±0.3	−1.19	−0.44	[3.04] s	
	14.90±0.3s	7.78	2.88	0.55	(0.5)
	8.17±0.3q	1.05	0.39		
B(s^2p, V_1)	3.75±0.3	−3.37	−1.25		
(sp^2, V_3)	4.21±0.3	−2.91	−1.08		
	10.28±0.3s	3.16	1.17		
	6.23±0.3q	−0.89	**−0.33**		
Be(sp, V_2)	3.06±0.2	−4.06	−1.51		
	6.33±0.2s	−0.79	−0.29		
	4.69±0.2γ	−2.43	**−0.90**		
Li(s, V_1)	2.86±0.2s	−4.26	−1.58		
S				(0.43)	0.68 (if 92° angle in H_2S)
P				(0.10)	0.36 (if 98° angle in PH_3)
As				—	0.10 (if 96° angle in AsH_3)

Notes for Table I. In *column* (*b*), the electroaffinities are all of the first stage type (one-half the energy difference between a singly-charged positive and negative ion each in the same valence state V_{l-1} where l is as given in column (*a*)), except those marked II. The latter are second-stage electroaffinities (one-fourth the energy difference between O^{++}, V_0 and $O^{=}$, V_0 or N^{++}, V_1 and $N^{=}$, V_1). The electron added or removed is a p electron, except in the cases marked s or q. For the s–p hybrid types q, the electroaffinities given are obtained from a weighted mean of s and p values (1 : 3 weight for sp^3, 1 : 2 for sp^2 and sp^4, 1 : 1 for sp). This method is not quite right* for q in all cases, but probably nearly enough so, since all values are rather rough. Necessary numerical data were taken from Table IV, except the electron affinity of H (0.715 volt), calculated quantum-mechanically by E. A. Hylleraas (Zeits. f. Physik **65**, 209 (1930)). The values in *column* (*e*) are from Pauling's paper[2] (units = volts[½]), except the s and p values for carbon, given in brackets; these have been obtained by applying to the s and p values in column (*d*) the same correction (0.16) that is needed to make the q value in column *d* agree with the thermal (presumably q) value in column (*e*). It is thought that the column (*e*) values thus obtained are likely to be more trustworthy than the column (*d*) values. The values in *column* (*f*) are from electric moment data and are in electric moment units, based on compounds H_mX;[5] Malone's value of 1.32 for O, which was based on an assumed HOH angle of 90° in H_2O, has here been corrected in accordance with Mecke's band spectrum determination of this angle as 104° 40′. In *column* (*d*) the data of *column* (*c*) have been divided by 2.70 to assist comparison with columns (*e*) and (*f*). Values in parentheses in columns (*e*) and (*f*) are uncertain; the value in column (*e*) for iodine also appears somewhat uncertain. All values for *polyvalent* elements in columns (*b*), (*c*) and (*d*) are distinctly uncertain, mainly because of the uncertainty of the electron affinity data available for these elements; rough estimates of uncertainty are given in column (*b*). *Added in proof:* If we use (c) ÷2.75 for column (*d*), the values 2.01, 0.98, 0.70 and 0.40 are obtained for F, Cl, Br, I, in close agreement with column (*e*).

$\psi(A^-B^+)$ contributions in building up a good wave function for a moderately polar molecule, e.g., HCl. Even in cases like NaCl, it may not always be wise to neglect the $\psi(Na^-Cl^+)$ term.

The "absolute electronegativities" $(I+E)/2$ for H, F, Cl, Br, I, and other atoms are given in Table I. Taking $I+E$ for H, we get 14.25 volts. For the other atoms, it is clear that the ordinary minimum ionization potentials and electron affinities must be replaced by corrected values. This we see on considering Eq. (1) as applied, for example, to HCl. ψ_{AB} for (the normal state of) HCl is of the $^1\Sigma^+$ type; this is to be built partly from H+Cl, partly from $H^+ + Cl^-$ and from $H^- + Cl^+$. For $H^+ + Cl^-$, there is no difficulty, Cl^- being in a ^1S state which necessarily gives $^1\Sigma^+$ on combination with H^+. In the case of $H^- + Cl^+$, H^- is $1s^2$, ^1S, but Cl^+, if we use its normal state, is s^2p^4, ^3P. Now $^3P(Cl^+) + {}^1S(H^-)$ can give only triplet states of HCl. [The rule that $^3A + {}^1B$ cannot give ^1AB, but only ^3AB, is no longer strict for heavy atoms like I, but nevertheless still holds approximately there in the sense that ψ_{AB}, which is ^1AB in the case we are considering, should still contain only rather small contributions from $(^3A^+) + (^1B^-)$.]

* See reference 6.

With $H^-(^1S)$ we must then use a singlet state or states of Cl^+. There are two such states of low energy, namely, ^1D and ^1S of s^2p^4. To calculate the proper I for Cl, we should take a value corresponding to some sort of average of the ^1D and ^1S of Cl^+.

The nature of this average can be determined by observing that the four chlorine outer-shell p electrons ($3p$) which are not used for valence purposes in HCl are necessarily in the $3p\pi$ condition ($m_l=\pm1$). The two electrons which form the bond are in the σ condition ($m_l=0$). These statements apply to all three of the terms $\psi(H-Cl)$, $\psi(H^+Cl^-)$, $\psi(H^-Cl^+)$ which make the principal contributions to ψ_{HCl}. The electronic structure of HCl may be described as $1s^22s^22p^63s^23p\pi^4\sigma^2$, all but the last two electrons belonging definitely to the Cl atom. In $\psi(H-Cl)$, one σ electron is $3p\sigma$ of Cl, the other is $1s$ of H; in H^+Cl^-, both σ electrons are $3p\sigma$ of Cl^-; in H^-Cl^+, both are $1s$ of H. We are now interested in H^-Cl^+; we see that the proper state of Cl^+ for union with H^- is $\cdots\cdots\cdots 3p\pi^4$, which is a singlet state ($^1\Sigma^+$ in fact). Unlike ^1D and ^1S, however, this is not a real state of uncombined Cl^+; nevertheless it has a meaning for *combined* Cl^+.

It belongs to the category of "valence states" (cf. section C, below). It is a valence state of type $s^2p\pi^4$, V_0 (here V_0 means zero valence in respect to homopolar bonding). Its energy will be found under the heading $s^2\pi^2\pi^2$, V_0 in Table III and s^2p^4, V_0 in Table IV. This has been estimated with the help of a method of Slater,[4] and is found to be between the energies of ^1D and ^1S, as expected. Although there are some difficulties in applying the method (cf. Table III), and although spectroscopic data on the ^1D and ^1S states are available only for F (not for Cl, Br, I), it has been possible to estimate the desired I values for F, Cl, Br, and I with an error which probably does not exceed ±0.5 volt at most. Using these corrected I values and the ordinary E values, we get the absolute electronegativities given in Table I. [Actually, I and E values for the valence state s^2p^5, V_1 of the halogen, given in Table IV, have been used, instead of the slightly different I and E values for the normal state s^2p^5, $^2P_{1\frac{1}{2}}$; but the sum $I+E$ is the same.][4a]

Besides the "absolute electronegativities" just obtained, the *relative* electronegativities referred to hydrogen as zero are given in Table I, and are seen to behave in a reasonable way. It may be noted that if we had used the ordinary ionization potentials of the halogens, this would not be the case; for example, the value for iodine relative to hydrogen would be negative. Comparing the relative electronegativities here obtained with those found by Pauling from thermal data, it is found (cf. Table I, columns d and e) that the two sets of values are proportional within the uncertainties of the thermal-data scale and of the I and E data. A similar agreement is found (column f) with another scale of relative electronegativities, based on electric moments.[5]

The agreements just found, even though probably to some extent fortuitous, indicate that the present "absolute" scale is at least roughly correct for univalent atoms. Granting this, the fact that "absolute" electronegativies are at least roughly proportional to the quantity $(I+E)$ gives new insight into the physical interpretation of the concept of electronegativity.

If the present method of calculating absolute electronegativies is a good one, the scale can readily be extended almost immediately to univalent electropositive atoms (Li, Na, K, $\cdots$, Cu^I, Ag, Au^I, perhaps Tl^I, etc.). The necessary I values are known, while the electron affinities are doubtless small enough so that even the uncertain estimates which can be made of their

[4] J. C. Slater, Phys. Rev. **34**, 1293 (1929). J. H. Van Vleck, Phys. Rev. **45**, 405 (1934) has recently given a simpler method of getting the energy formulas.

[4a] At this point a question which might be raised will be answered. Why cannot we make use of excited triplet states of H^-, e.g., $1s2s$, ^3S, in combination with ^3P of Cl^+, since $^3S+^3P$ is capable of giving $^1\Sigma^+$ of HCl? The energy of $1s2s$, ^3S and other triplet states should be only about 0.7 volt higher than that of $1s^2$, ^1S, if we assume zero electron affinity for nx, $n>1$, in H^-, and the total energy of $^3S+^3P$ would be considerably lower than that of $(1s^2, ^1S)$ plus $(3p^4, ^1D$ or $^1S)$. It is true that such terms should contribute to $^1\Sigma^+$ of HCl, but these contributions would probably be small compared with the others, for the reason that Cl^+ (^3P) would give rise to an electron configuration $3p\pi^23p\sigma$ or $3p\pi^23p\sigma^2$, instead of the required $3p\pi^4$. The question just raised and answered for H^- has its analogue for Cl^- and the others, although because of the much larger electron affinity for formation of unexcited Cl^-, etc., the (unstable) excited states are relatively much higher in energy than for H^-, and so need much less to be considered.

[5] H. M. Smallwood, Zeits. f. physik. Chemie **B19**, 242 (1932). J. G. Malone, J. Chem. Phys. **1**, 197 (1933); M. G. Malone and A. L. Ferguson, J. Chem. Phys. **2**, 99 (1934).

values should give fairly satisfactory results (cf. Li in Table I, for which $I=5.37$, E (est.) $=0.34$). With this inclusion of electropositive atoms (which give negative electronegativities relative to H), the scale might perhaps better be described as a scale of electroaffinity rather than of electronegativity,—if we may return to a somewhat obsolescent word. Essentially correct results might probably be expected for all univalent *s*-valent atoms if their electroaffinities are taken proportional to their ionization potentials, with the same proportionality constant as for Li.

B. Polyvalent Atoms

We may next consider whether, and, if so, how, the present scale of electroaffinities can be extended to polyvalent atoms. The two other scales (thermal and electric-moment), which have already been developed for a few polyvalent atoms (but only for the case of single bonds), can serve here as an empirical guide and check.

As an example of a polyvalent atom, we may consider oxygen. Instead of Eq. (1) we now have, for a compound AOB, or more simply A_2O, the following (we neglect terms such as $\psi(A^+OA^-)$, $\psi(A-A, O)$, etc.):

$$\psi(A_2O)=a\psi(A-O-A)+b\psi(A-O^-A^+)+c\psi(A-O^+A^-)+d\psi(A^+O^=A^+)+e\psi(A^-O^{++}A^-). \quad (4)$$

Suppose, for purposes of argument, that the energy required to produce $A+O^++A^-$ from $A+O+A$ should be the same as to produce $A+O^-+A^+$, and to produce $2A^++O^=$ the same as to produce $2A^-+O^{++}$. [Actually, the coexistence of these two relations is not likely to be fulfilled more than approximately, at best.] Then we should have

$$I_O-E_A=I_A-E_O, \quad \text{hence} \quad I_O+E_O=I_A+E_A,$$

as in Eqs. (2), (3). Also we should have

$$II_O-2E_A=2I_A-EE_O; \quad \text{and}$$

$$(II_O+EE_O)/2=I_A+E_A, \quad (5)$$

where II_0, EE_0 are the double ionization potential and electron affinity ($O\rightarrow O^{++}$, $O\rightarrow O^=$). If the net energy of coming together, undeformed, to give A–O distances equal to those in the actual molecule A_2O, should be the same for AO^+A^- as for AO^-A^+, and for $A^+O^=A^+$ as for $A^-O^{++}A^-$, and if also

$$\int\psi(A-O-A)H\psi(A-O^+A^-)d\tau \approx \int\psi(A-O-A)H\psi(A-O^-A^+)d\tau,$$

etc., then we might define $\frac{1}{2}(I_O+E_O)$ and $II_O+EE_O)/4$, respectively, as the *first-stage* and *second-stage electroaffinities* of the O atom. [Note that the energies of coming together of AO^-A^+, $A^+O^=A^+$, etc., would be more complicated here than in the case earlier considered of a molecule AB; there would be energies of interaction between the two A^+ atoms, or the A and A^+, for example; hence the likelihood of correctness of the suppositions just made is harder to check than in the case of AB.]—A similar need for considering both first- and second-stage electroaffinities occurs, it may be noted, in double-bonded molecules, e.g. BeO.

The values of I_O and II_O must, of course, be chosen to correspond to the right "valence states" of O^+ and O^{++}, which are $O^+(s^2p^3, V_1)$ and $O^{++}(s^2p^2, V_0)$, respectively. This is because in O^++H^-+H, the O must be in a doublet state (V_1, intermediate between ^2D and ^2P of s^2p^3), since only in this way can the spins of O^+, H^-, and H (respectively, $\frac{1}{2}$, 0, $\frac{1}{2}$) combine to give the zero resultant spin characteristic of H_2O in its normal state. It may be noted that here the O^+ forms one homopolar bond (with the neutral H), one ionic bond with the H^+. In the case of $O^{++}+H^-+H^-$, the O has to be in a singlet state (V_0, intermediate between ^1D and ^1S: cf. the valence state of Cl^+ in H^-Cl^+, above), since both H ions are in singlet states (zero spin). The O^- and $O^=$ ions in H^+HO^- and $H^+H^+O^=$ are respectively in the states s^2p^5, $^2P=V_1$ and s^2p^6, $^1S=V_0$.

If one knew that *b* and *c* in Eq. (4) were much larger than *d* and *e*, one might expect the first-stage electronegativity to agree with Pauling's scale value; or if *d* and *e* were much larger than *c* and *d*, the second-stage electronegativity might be expected to show such an agreement. If *b* and *d* should be larger than *c* and *e*, it is difficult to say what might be expected. If *b*, *c*, *d*, *e* are all of since sp^4 has one *s* and two *p* valence electrons), it would be possible to get agreement with the

comparable magnitude, some average of first- and second-stage electronegativities might be suitable. The following data suggest that the actual situation may be of this nature.

Table I shows that the estimated first-stage and second-stage electronegativities of O (whose values, it should be noted,—cf. Table I,—are somewhat uncertain, because of uncertainty in the electron affinities) do not differ very greatly, and that their average agrees fairly well with the electronegativities estimated from thermal and electric moment data. This is encouraging.

For nitrogen we ought to consider a first-stage, a second-stage, and a third-stage electronegativity, but it is impossible to estimate the electron affinity for the process $N \rightarrow N^{\equiv}$ with any accuracy. The value for $N \rightarrow N^{=}$ is also a mere guess, and that for $N \rightarrow N^{-}$ is decidedly uncertain. According to Table I, both first-stage and second-stage electronegativities (although the value for the latter is doubtful) give values which are definitely too low compared with thermal and electric moment data if, as is usual, we assume the N atom in its ordinary valence state (V_3) to have the normal-state configuration s^2p^3. For the ions N^+ and N^{++}, as is easily shown, we should then use the valence states s^2p^2, V_2, and s^2p, $^2P = V_1$, respectively. The valence state s^2p^2, V_2, it may be noted ($s^2p_xp_y$ in Table II), is neither a triplet nor a singlet state, but really a mixture of both, with emphasis on the triplet, however.—It appears, incidentally, that the third-stage electronegativity for s^2p^3, V_3, if we may extrapolate from the first- and second-stage values, might agree with the empirical data.

There is, however, another possibility, namely, that we ought to consider not the electronegativity of the s^2p^3 configuration, but something intermediate between this and that of the sp^4 configuration. The sp^4, like s^2p^3, gives only three valence bonds, but because of a partial mixing of s with p valence, can give stronger bonds. One can calculate an s as well as a p electronegativity for sp^4 by taking I and E; the first-stage s and p electronegativities for sp^4 of nitrogen are given in Table I. It will be seen that by taking a suitably weighted mean of first-stage electronegativities for s^2p^3 (here only p valence and electronegativity are possible) and for sp^4 (here we should take a 1 : 2 weighted mean of s and p electronegativities, empirical values. On calculation, one finds that a 56 percent participation of s^2p^3 and 44 percent participation of sp^4 in the nitrogen valence would give a first-stage electronegativity agreeing with the thermal value 0.95. Since such a relative participation of s^2p^3 and sp^4 appears not unreasonable, we have some support for the attractive possibility that we may get nearly correct absolute electronegativities by using just first-stage values.

This idea gains further support, as we shall see, from the evidence on carbon. In the case of oxygen, it is also not unreasonable. The calculated first-stage electronegativity is there lower than the empirical values, which might be explained by a need of considering the second-stage electronegativity too; but it seems quite possible that a small participation of sp^5 instead of exclusively s^2p^4, in the bivalence of oxygen, might serve to account for the discrepancy on the basis of first-stage electronegativities alone. Without denying that higher-stage electronegativities may be important and possibly needed for best results,—but noting that, fortunately, they seem not to differ radically from first-stage values,—we shall from now on assume that approximately correct values of the true effective electronegativities of atoms can be obtained by using first-stage electronegativities.

Turning to carbon, we find that in its normal electron configuration s^2p^2 with valence two, this element should be decidedly electropositive, i.e., below hydrogen on the electronegativity scale. Carbon with valence four, however (sp^3, V_4), according to our method, if we take the first-stage electronegativity averaged over the one s and three p valences, is electronegative relative to hydrogen, the result (0.39 ± 0.1) here obtained being in rather good agreement with the value (0.55) given by Pauling (cf. Table I). The process of averaging, with weight 1 : 3, the s and p electroaffinities of the valence state sp^3, V_4 should probably be nearly equivalent to calculating the first-stage electronegativity for the Pauling-Slater tetrahedral or q type of orbital for the valence state q^4, V_4 (cf. Van Vleck[6]

[6] J. H. Van Vleck, J. Chem. Phys. **2**, 22 (1934). (Van Vleck considers a range of valence states of carbon from q^4, V_4 (complete s–p hybridization, $\mu = \frac{1}{4}$) to sp^3, V_4 (no hybridization, $\mu = 1$ in Van Vleck's Eq. (7).)

for a discussion of the valence states sp^3, V_4 and q^4, V_4). The good agreement just noted gives added support to the present method, and gives considerable confidence that it may be extended to other cases, a few examples of which are given in Table I.

In connection with the use of first-stage electronegativities for polyvalent atoms, a consideration of diatomic radicals may prove instructive. In the case of the single O−H bond in the radical OH, for example, the proper electronegativity for the O atom is found to be just the first-stage electronegativity, if we apply the reasoning used above for the type AB; the result is unaffected by the potential second valence of O. If in H_2O each of the two single bonds is very similar to the one bond in OH, as is generally supposed, then the first-stage electronegativity of O should be appropriate for O in H_2O as well as in OH. A similar result should hold in other cases. (This would still be true even if the actual A−B bond in a diatomic radical should differ from that in a saturated molecule. In CH, for instance, the actual C−H bond may be formed almost wholly by a carbon p orbital whereas in CH_4 the C−H bonds may be constructed with the help of q carbon orbitals. Nevertheless, each C−H bond in CH_4 might closely resemble the hypothetical case of a C−H single bond formed in C−H by a carbon q electron, justifying the use of a first-stage q electronegativity for carbon in CH_4.)

A variety of applications of electronegativity values calculated by the present method can be made. Because of the intimate relation of electroaffinity to thermal data and to electric moments, as shown by the setting up of electronegativity scales on the basis of the latter, various predictions in regard to dipole moments, bond moments, and energies of formation might be made from electroaffinities calculated by the present method. For instance, single molecules of LiI, BeO, and HF should have bonds of about equal polarity and also of about equal electric moment, if the parallelism of electric moments to electronegativity differences continues to hold with the more electropositive elements. LiH molecules should be intermediate between HCl and HF in polarity. If compounds with divalent carbon could be isolated, the carbon should be positive relative to hydrogen; this would probably be expected in the radical CH_2, whereas in CH_4 the carbon is supposed to be relatively negative.

No attempt will be made here to make extensive predictions; the method by which this can be done for heats of formation of compounds can be seen from Pauling's paper.[2] Very roughly quantitative predictions could be made by using the electronegativities in column (d) of Table I, which have been reduced to approximately the same numerical values as Pauling's scale. Many more predictions could be made by working out the scale values for all the chemical elements. In many cases, however, this cannot yet be done satisfactorily because of insufficient spectroscopic data. Most of the scale values in Table I can be made more accurate when additional or more reliable spectroscopic data and, in particular, more accurate electron affinities become available. It must also be remembered that the scale is as yet largely empirical in character, and, especially for polyvalent atoms, needs further investigation and testing from both theoretical and experimental standpoints.

A result which should hold quite generally in cases where valence can be varied in steps of two by exciting inner electrons is that, for a given atom, electronegativity increases with increasing valence. In other words, the lowest valence is the most electropositive. This is perhaps nothing new; what is new here is the scale for measuring these differences. For example, trivalent boron is 0.33 unit electropositive relative to hydrogen in Table I, column c, while monovalent boron, if it were stable, would be 1.25 units electropositive. A similar result is to be expected in other cases, e.g., Tl, where both valences are actually realized. Similarly divalent carbon is 0.64 unit electropositive, tetravalent carbon 0.39 unit electronegative; a similar difference is to be expected in Sn, where both valences are easily realized. The difference here results chiefly from the higher electronegativity of s than of corresponding p valences. In more complex atoms, d valences also enter. A calculation of electroaffinities for the various valence states of Cu, Ag, Au, Zn, Cd, Hg would be interesting, although spectroscopic data are somewhat incomplete.

TABLE II. *Interaction energies for atomic states belonging to configurations $1s^2 2s^m 2p^n$* (cf. also Table IIA).

State	G_1	G_2	State	G_1	G_2	State	G_1	G_2
s^2, $^1S=V_0$	0	0	sp^3 See Table IIA			$(s^2)p^4$, ^3P	−4	−15
sp, ^3P	−1	0	$(s^2)p^3$, ^4S	−3	−15	^1D	"	−9
^1P	1	0	^2D	"	−6	^1S	"	0
V_2	−½	0	^2P	"	0	x^2yz, V_2	"	−13½
$(s^2)p$, $^2P=V_1$	−1	0	xyz, V_3	"	−10½	$\pi^2\pi\sigma$, V_2	"	−13½
sp^2, ^4P	−2	−5	$\pi\pi\sigma$, V_3	"	−9	$\sigma^2\pi\pi$, V_2	"	−12
^2P	1	−5	x^2y, $\sigma^2\pi$,	"	−3	$\pi^2\pi^2$, x^2y^2, V_0	"	−6
^2D	−1	1	$\pi^2\pi$, V_1					
^2S	−1	10	$\pi^2\sigma$, V_1	"	−6	$\sigma^2\pi^2$, V_0	"	−9
sxy, $s\pi\sigma$, V_3	−1	−3½	sp^4, ^4P	−3	−15	sp^5, ^3P	−3	−20
			^2P	0	−15	^1P	−1	"
$s\pi\pi$, V_3	−1	−2	^2D	−2	−9	sx^2y^2z, V_2		
sx^2, $s\sigma^2$, V_1	−1	4	^2S	"	0	$s\pi^2\pi^2\sigma$, V_2	−2½	"
$s\pi^2$, V_1	−1	1	sx^2yz, V_3	"	−13½	$s\pi^2\pi\sigma^2$, V_2		
$(s^2)p^2$, ^3P	−2	−5	$s\pi^2\pi\sigma$, V_3	"	−13½	$(s^2)p^5$, $^2P=V_1$	−5	−20
^1D	"	1	$s\sigma^2\pi\pi$, V_3	"	−12	sp^6, $^2S=V_1$	−3	−30
^1S	"	10	$s\pi^2\pi^2$,	"	−6	$(s^2)p^6$, $^1S=V_0$	−6	−30
xy, $\pi\sigma$, V_2	"	−3½	sx^2y^2, V_1					
$\pi\pi$, V_2	"	−2	$s\sigma^2\pi^2$, V_1	"	−9			
x^2, σ^2, V_0	"	4						
π^2, V_0	"	1						

Explanation of Table II: (*a*) The symbols s, p, x, y, z, π, $\pi\pi$, π^2, σ, here respectively denote $2s$, $2p$, $2p_x$, $2p_y$, $2p_z$, $2p\pi(2p_{+1}$ or $2p_{-1})$, $2p\pi_+ 2p\pi_-$, $(2p\pi_+)^2$ or $(2p\pi_-)^2$, $2p\sigma(2p_0)$, while (s^2) indicates *either* $(2s)^2$ or nothing. The letter V denotes a "valence state," whose valence is given by the subscript. G_1 means $(1/3)G^1(2s, 2p)$, G_2 means $(1/25)G^2(2p, 2p)$ of Slater.[4] The numbers in the columns headed G_1 and G_2 give the numerical factor with which G_1 or G_2 appears in the energy expression for the state in question.

(*b*) Certain terms which are constant for any one electron configuration have been omitted from Tables II and IIA. The omitted terms which come from integrals of the types which Slater calls J's and K's are given by the following formula: $F^0(1s,1s)+\alpha F^0(2s,2s)+2mF^0(1s,2s)+2nF^0(1s,2p)+mnF^0(2s,2p)-mG^0(1s,2s)-(n/3)G^1(1s,2p)+\beta G^0(2p,2p)$, where $\alpha=1$ if $m=2$, otherwise $\alpha=0$, and where $\beta=0, 0, 1, 3, 6, 10, 15$, for $n=0, 1, 2, 3, 4, 5, 6$, respectively.

(*c*) The way in which β, and the coefficients of G_1 and G_2 in Table II, were obtained is illustrated by Table IIA. The remaining F's and G's in the formula just given under (*b*) correspond to J's and K's involving pairs of electrons not both of $2p$ type; in connection with them cf. Slater's tables, reference 4, p. 1312.

C. Appendix: Interaction Integrals and Energy Data for Configurations $1s^2 2s^m 2p^n$

In the following Table II are given the numerical factors with which certain interaction integrals called J's and K's, or F's and G's, occur in Slater's method[4] of approximating the energies of the states of complex atoms. The total energy of an atom in a given state is approximately equal to the sum of certain terms which are constant for a given electron configuration, plus others which vary from one state to another of the configuration.

In addition to the actual atomic states associated with the various electron configurations in Table II, whose energies have already been given by others,[6a] energy expressions are also tabulated for certain "*valence states*." The term valence state, introduced by Van Vleck,[6] describes a certain hypothetical state of interaction of the electrons of an atomic electron configuration. In formulating these, we shall here most often use the classification $2p_x$, $2p_y$, $2p_z$ for the $2p$ orbitals

$$(2p_z \equiv 2p_0,\ 2p_x = 2^{-\frac{1}{2}}(2p_{+1}+2p_{-1}),$$
$$2p_y = 2^{-\frac{1}{2}} i^{-1}(2p_{+1}-2p_{-1})).$$

Still other types of valence states, involving various hybrid orbitals formed by mixing $2s$ and $2p$, could be given, but are omitted from the

[6a] Slater, Condon and Shortley, in part, and recently Van Vleck (Reference 4, Eqs. 22, 38).

TABLE IIA. *Illustration of derivation of results in Table II.*

State	$J_{\sigma\sigma}$	$J_{\sigma\pi}$	$J_{\pi\pi}$	$K_{\sigma\pi}$	$K_{\pi\pi}$	G_1	$G^0(2p, 2p)$	G_2
sp^3, ^5S	0	2	1	−2	−1	−3	3	−15
^3S	−1	4	0	−1	0	1	"	−15
^3D	0	2	1	−1	0	−2	"	−6
^1D	0	2	1	−1	0	0	"	−6
^3P	1	0	2	0	−1	−2	"	0
^1P	1	0	2	0	−1	0	"	0
$sxyz$, V_4	0	3	0	$-1\frac{1}{2}$	0	$-1\frac{1}{2}$	"	$-10\frac{1}{2}$
$s\pi\pi\sigma$, V_4	0	2	1	−1	$-\frac{1}{2}$	$-1\frac{1}{2}$	"	−9
sx^2y, $s\sigma^2\pi$, $s\pi^2\pi$, V_2	1	2	0	−1	0	$-1\frac{1}{2}$	"	−3
$s\pi^2\sigma$, V_2	0	2	1	−1	0	$-1\frac{1}{2}$	"	−6

Explanation: Below each heading $J_{\sigma\sigma}$, etc., is given the factor by which this integral is to be multiplied in getting the energy of the state in question: these numbers are determined by Slater's method,[4] modified in the case of the *valence* (unpaired) *electrons* in *valence states* in that $-\frac{1}{2}K$ is put down for the K interaction of each two valence electrons (see text). The symbols $J_{\sigma\sigma}$, $J_{\sigma\pi}$, $J_{\pi\pi}$, $K_{\pi\sigma}$, $K_{\pi\pi}$, and $G_1 \equiv (1/3)G^1(2s, 2p)$ refer, respectively, to Slater's $J(2p_0, 2p_0)$, $J(2p_{\pm1}, 2p_0)$, $J(2p_{\pm1}, 2p_{\pm1})$, $K(2p_{\pm1}, 2p_0)$, $K(2p_{\pm1}, 2p_{\pm1})$, and $K(2s, 2p_{0,\pm1})$, and respectively reduce (see Slater's tables,[4] p. 1312) to $F^0(2p, 2p)+(4/25)F^2(2p, 2p)$; $F^0(2p, 2p)-(2/25)F^2(2p, 2p)$; $F^0(2p, 2p)+(1/25)F^2(2p, 2p)$; $(3/25)G^2(2p, 2p)$; $(6/25)G^2(2p, 2p)$; $(1/3)G^1(2s, 2p)$, with $F^0(2p, 2p)=G^0(2p, 2p)$ and $F^2(2p, 2p)=G^2(2p, 2p)$ here (equivalent p electrons). By using these relations for the J's and K's, the results in the last three columns are obtained. The results in Table II were obtained in the same way. A simpler method for the ordinary atomic states has recently been given by Van Vleck (reference 4, Eqs. (22) and (38)). Table IIA gives only those J's and K's (including $G_1=K(2s, 2p)$) which vary for different states of sp^3.

tables below; such states, often important for atoms having both s and p valences, are discussed by Van Vleck.[6]

It is evident that

$$J(2p_z, 2p_z)=J(2p_y, 2p_y)=J(2p_x, 2p_x),$$

since in the x, y, z classification $2p_x$, $2p_y$, $2p_z$ are equivalent; these integrals may be denoted $J_{\sigma\sigma}$. It is then easily shown[6b] that $J(2p_x, 2p_y)=J(2p_x, 2p_z)=J(2p_y, 2p_z)=J(2p_0, 2p_{+1})$, which may be denoted $J_{\pi\sigma}$; and that $K(2p_x, 2p_y)=K(2p_x, 2p_z)=K(2p_y, 2p_z)=K(2p_0, 2p_{+1})$, which may be denoted $K_{\pi\sigma}$. Hence the integrals for electron configurations expressed in terms of $2p_x$, $2p_y$, $2p_z$ can be tabulated under the headings $J_{\sigma\sigma}$, $J_{\pi\sigma}$, $K_{\pi\sigma}$ in Table II (cf. Table IIA).

[6b] Cf. Slater, Reference 4, p. 1133.

A "valence state" is an atom state chosen so as to have as nearly as possible the same condition of interaction of the atom's electrons *with one another* as when the atom is part of a molecule. The electrons in question may be classified as non-valence electrons and valence electrons. The non-valence electrons are usually in pairs (e.g., $2p_x^2$ in the configuration $1s^22s^22p_x^22p_y2p_z$), in which case the m_s values of the two electrons are necessarily opposite in sign so that (cf. Slater) the coefficient of the integral $K(2p_x, 2p_x)$ is zero.

A valence state of an atom is one in which the latter's valence electrons behave *toward one another* as if each were paired somehow with a valence electron of a foreign atom, but not with any valence electron of the given atom. Before going further, we note that this question of pairing of the electrons in a valence state of an atom affects only the integrals K, and then only of electrons not intra-atomically paired. The J's, for a given detailed electron configuration specified in terms of m_l values or of the x, y, z classification (e.g., $2p_x^22p_y2p_z$ or $2p_{+1}2p_{-1}(2p_0)^2$), do not depend on the m_s values of the electrons.

The correct contribution of the K's to the energy for a valence state of a given atom is obtained by writing $-\frac{1}{2}K(i,j)$ for every combination (i,j) of the valence electrons of the given atom taken two at a time; this result, or essentially this, has been obtained by Slater and others.[6b, 7] Any *unpaired* non-valence electron which may be present can be treated for this purpose as a valence electron; this case of unpaired non-valence electrons is of interest when we consider certain ionization processes, e.g., removal of a non-valence electron from a fluorine atom which belongs to an F_2 molecule.

The result just stated is based on the fact that the K interaction between two electrons i,j each in a definite orbital state (definite n, l, and m_l or n, l, and x, y, z, classification) is zero if the two electrons have opposite m_s values $(+\frac{1}{2}, -\frac{1}{2})$, but equal to $-K(i,j)$ if both have the same m_s value. Now any unpaired electron in a valence state (including unpaired non-valence electrons) is in a condition such that the probability that its

[7] Cf. J. C. Slater, Phys. Rev. **38**, 1109 (1931), discussion of several electrons with only spin degeneracy. The results given there can of course be used even if two or more electrons are on the same atom.

TABLE III. *Approximate energies of valence states in volts.*

State	Atom or ion; normal state		Energy (above normal state energy)	Method of estimation [N. B. In many cases averages were used (cf. e.g. s^2xy, V_2) because Slater's relations (Table II) do not hold well]
s^2, V_0	s^2, ^1S		All 0.00	
sp, V_2	s^2, ^1S:	Li^-	[0.97]	Extrapolated from Be, B^+
		Be	3.35	sp, ^3P plus $(^1P-^3P)/4$
		B^+	5.70	Ditto
		C^{++}	8.00	"
xy, V_2	s^2, ^1S:	Li^-	[2.52]	Extr. from Be, B^+
		Be	7.50	p^2, ^3P plus $1\frac{1}{2}G_2$ (est. $6G_2=6000$)
		B^+	12.43	Same method (est. $6G_2=8560$)
x^2, V_0	s^2, ^1S:	Li^-	[3.07]	Extr. from Be, B^+
		Be	(8.43)	xy, V_2 plus $7\frac{1}{2}G_2$ (see xy, V_2)
		B^+	(13.75)	Ditto
s^2p, V_1	s^2p, ^2P		All 0.00	
sxy, V_3	s^2p, ^2P:	Be^-	[2.55]	Extr.
		B	5.35	$^2D-4\frac{1}{2}G_2$; $9G_2=(8950)$ by extr. from C^+ etc.
		C^+	8.15	$^2D-4\frac{1}{2}G_2$; $9G_2=17{,}780$, ave. value from ^4P, ^2P, ^2D, ^2S
		N^{++}	10.88	Same method; $9G_2=25{,}790$
		O^{+++}	13.63	Same method; $9G_2=32{,}990$
sx^2, V_1	s^2p, ^2P:	Be^-	[2.60]	Extr.
		B	6.28	$^2D+3G_2$; G_2 as for sxy, V_3
		C^+	9.97	Ditto
		N^{++}	13.52	"
		O^{+++}	17.02	"
xyz, V_3	s^2p, ^2P:	C^+	(18.0)	p^2, $^4S+\frac{1}{2}(^2D-^4S)$
x^2y, V_1				
s^2xy, V_2	s^2p^2, $^3P_0$: (see note *b*)	B^-	[0.28]	Extr.
		C	0.49	Aver. of $(^1D-^3P)/4$ and $(^1D-^3P)/4-\frac{1}{2}(^1S-^1D)$
		N^+	0.66	Ditto
		O^{++}	0.89	"
		F^{+++}	(1.07)	"
s^2x^2, V_0	s^2p^2, $^3P_0$:	B^-	[0.90]	Extr.
		C	1.80	s^2p^2, ^1D plus aver. of $(^1S-^1D)/3$ and $\frac{1}{2}(^1D-^3P)$
		N^+	2.73	Ditto
		O^{++}	3.60	"
		F^{+++}	(4.43)	"
$sxyz$, V_4	s^2p^2, $^3P_0$:	B^-	[4.66]	Extr.
		C	8.16	$^3D+\frac{1}{2}G_1-4\frac{1}{2}G_2$; $\frac{1}{2}G_1=[10{,}460]$; $6G_2=(11{,}200)$ from ^3D, ^3P and extr.
		N^+	11.59	$^3D+\frac{1}{2}G_1-4\frac{1}{2}G_2$; $\frac{1}{2}G_1=13{,}644$ and $6G_2=16{,}040$; ave. values from ^3S, ^3D, ^3P, ^1S, ^1D, ^1P
		O^{++}	15.09	Same method; $\frac{1}{2}G_1=16{,}973$ and $6G_2=20{,}055$
		F^{+++}	18.51	$^3D+\frac{1}{2}G_1-4\frac{1}{2}G_2$; $\frac{1}{2}G_1=20{,}448$ and $6G_2=24{,}610$ from ^3S, ^3D, ^3P, ^1D, ^1P and Extr.
sx^2y, V_2 = $s\sigma^2\pi$, V_2 = $s\pi^2\pi$, V_2	s^2p^2, $^3P_0$:	B^-	[5.68]	Extr.
		C	9.89	$^3D+\frac{1}{2}G_1+3G_2$; G_1 and G_2 as for $sxyz$, V_4
		N^+	14.06	Ditto
		O^{++}	18.19	"
		F^{+++}	22.30	"
x^2yz, V_2	s^2p^2, $^3P_0$:	N^+	[27.4]	Rough estimate
x^2y^2, V_0				
s^2xyz, V_3	s^2p^3, ^4S:	C^-	[0.79]	Extr.
		N	1.33	Aver. of $\frac{1}{2}(^2D-^4S)$ and $(^2D-^4S)-3(^2P-^2D)/4$
		O^+	1.85	Ditto
		F^{++}	2.35	"
s^2x^2y, V_1 = $s^2\sigma^2\pi$, V_1 = $s^2\pi^2\pi$, V_1	s^2p^3, ^4S:	C^-	[1.83]	Extr.
		N	3.06	s^2p^3, ^2D plus aver. of $\frac{1}{3}(^2P-^2D)$ and $(^2D-^4S)/3$
		O^+	4.29	Ditto
		F^{++}	5.45	"
$s^2\pi\pi\sigma$, V_3	s^2p^3, ^4S:	N	1.69	s^2p^3, ^2D minus aver. of $(^2D-^4S)/3$ and $\frac{1}{3}(^2P-^2D)$
		O^+	2.35	Ditto
$\pi^2\sigma$, V_1		O^+	3.32	Same as ^2D of s^2p^3
sx^2yz, V_3 = $s\pi^2\pi\sigma$, V_3	s^2p^3, ^4S:	C^-	[8.84]	Extr.
		N	(13.86)	sp^4, $^2D-4\frac{1}{2}G_2$, where $4\frac{1}{2}G_2=(8922)$ est. from O^+, F^{++}; and ^2D est. from O^+, F^{++}
		O^+	18.88	Ditto, with $4\frac{1}{2}G_2=(13{,}113)=$ aver. of $[\frac{1}{3}(^2P-^4P)-3(^2P-^2D)/4]$ and $\frac{1}{3}(^2S-^2D)$
		F^{++}	23.84	Ditto, with $4\frac{1}{2}G_2=(17{,}147)$ from ^4P, ^2P, ^2D and O^+
sx^2y^2, V_1 = $s\pi^2\pi^2$, V_1	s^2p^3, ^4S:	C^-	[9.81]	Extr.
		N	(15.69)	sp^4, $^2D+3G_2$, with G_2 as for sx^2yz, V_3
		O^+	21.57	Ditto
		F^{++}	27.37	"
x^2y^2z, V_1 = $\pi^2\pi^2\sigma$, V_1				
s^2x^2yz, V_2 = $s^2\pi^2\pi\sigma$, V_2	s^2p^4, $^3P_2$: (see note *b*)	N^-	[0.38]	Extr.
		O	0.67	Aver. of $(^1D-^3P)/4$ and $(^1D-^2P)-\frac{1}{2}(^1S-^1D)$
		F^+	0.95	Ditto
		Cl^+	(0.74)	From $(s^2xyz,V_2-s^2p^4,^3P_2)=(V_2-{}^3P_{center\ of\ gravity})+({}^3P_{c.g.}-{}^3P_2)$, with ${}^3P_{c.g.}-{}^3P_2=({}^3P_2-{}^3P_0)/3=0.04$, (0.17). (0.35) for Cl^+, Br^+, I^+; and $(V_2-{}^3P_{c.g.})$ est. roughly by assuming ratio of this quantity to ionization potential of atom is same as for F: e.g., for Cl^+, est. $(V_2-{}^3P_{c.g.})=0.70=(0.93/17.32)(12.96)$
		Br^+	(0.78)	
		I^+	(0.92)	
$s^2x^2y^2$, V_0 = $s^2\pi^2\pi^2$, V_0	s^2p^4, $^2P_2$:	O	2.81	s^2p^4, ^1D plus aver. of $\frac{1}{2}(^1D-^3P)$ and $(^1S-^1D)/3$
		F^+	3.87	Ditto
		Cl^+	(2.92)	Rough estimates for Cl^+, Br^+, I^+ made as for V_2 above
		Br^+	(2.79)	
		I^+	(2.69)	
sx^2y^2z, V_2 = $s\pi^2\pi^2\sigma$, V_2	s^2p^4, $^3P_2$:	N^-	[11.54]	Extr.
		O	17.08	sp^5, ^3P plus est. $(^3P-^1P)/4$ (*est.* $=15{,}120$)
		F^+	22.70	sp^5, ^3P plus $(^3P-^1P)/4$ $(^3P-^1P=75{,}574)$
		Ne^{++}	28.03	sp^5, ^3P plus est. $(^3P-^1P)/4$ (*est.*$=22{,}470$)
$x^2y^2z^2$, V_0 = $\pi^2\pi^2\sigma^2$, V_0				
$s^2x^2y^2z$, $V_1={}^2P$ = $s^2\pi^2\pi^2\sigma$, $V_1={}^2P$	s^2p^5, $^2P_{1\frac{1}{2}}$:	F	0.02	$(^2P_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}})/3$
		Cl	0.04	
		Br	0.15	
		I	0.31	
$sx^2y^2z^2$, $V_1={}^2S$ = $s\pi^2\pi^2\sigma^2$, $V_1={}^2S$				

Notes: (*a*) In the above table, values are given for most but not all cases where the necessary data on atomic energies are available either directly or with the help of fairly reliable interpolations or extrapolations. Data used in the calculations were taken from R. F. Bacher and S. Goudsmit, *Atomic Energy States;* additional data on C^+, N^+, N^{++}, O^{++}, O^{+++}, and on F^+, F^{++}, F^{+++} from B. Edlén, Zeits. f. Physik **84**, 746 (1933) and I. S. Bowen, Phys. Rev. **45**, 82 (1934).

(*b*) For s^2p^4, ^3P, corrections of $\frac{1}{2}(^3P_2-{}^3P_1)$ have been included to take care of the fact that the component $^3P_2$ is below the center of gravity of ^3P by that amount. For s^2p^2, ^3P, a correction of $2(^3P_2-{}^3P_0)/3$ has been applied to correct for the difference between $^3P_{center\ of\ gravity}$ and $^3P_0$.

TABLE IV. *Some ionization potentials and electron affinities (volts).* (Most values are only approximate. Valence states given here are only *xyz* states: cf. Table III; ionization potentials and electron affinities for removal of electrons from valence states having σ, π quantization can easily be obtained, when needed, with the help of Tables II, III. Removal of *s* electron is indicated by *s* in Ioniz. pot. column; in all other cases a *p* electron is removed.)

State of atom (or neg. ion)	State of pos. ion (or atom)	Ioniz. pot. (or el. aff.)
$Li^-(s^2, {}^1S=V_0)$	$Li(s, {}^2S=V_1)$	0.34†s
$Li(s, {}^2S=V_1)$	$Li^+({}^1S=V_0)$	5.37s
$Be^-(s^2p, {}^2P=V_1)$	$Be(s^2, {}^1S)$	−0.57†
(s^2p, V_1)	(sp, V_2)	2.78*s
(sp^2, V_1)	(sp, V_2)	0.18*
$Be(s^2, {}^1S)$	$Be^+(s, {}^2S=V_1)$	9.28s
(sp, V_2)	(s, V_1)	5.93*
(sp, V_2)	$(p, {}^2P=V_1)$	9.87*s
(p^2, V_2)	(p, V_1)	5.72*
$B^-(s^2p^2, {}^3P)$	$B(s^2p, {}^2P=V_1)$	0.12†
(s^2p^2, V_0)	(s^2p, V_1)	−0.78*
(s^2p^2, V_2)	(sp^2, V_3)	5.19*s
(sp^3, V_2)	(sp^2, V_3)	−0.21*
$B(s^2p, {}^2P=V_1)$	$B^+(s^2, {}^1S=V_0)$	8.28
(sp^2, V_3)	(sp, V_2)	8.63*
(sp^2, V_3)	(p^2, V_2)	15.36*s
$C^-(s^2p^3, {}^4S)$	$C(s^2p^2, {}^3P)$	1.37†
(s^2p^3, V_1)	(s^2p^2, V_2)	0.03*
(s^2p^3, V_3)	(sp^3, V_4)	8.74*s
(sp^4, V_3)	(sp^3, V_4)	0.69*
$C(s^2p^2, {}^3P)$	$C^+(s^2p, {}^2P=V_1)$	11.22
(s^2p^2, V_2)	(s^2p, V_1)	10.73*
(s^2p^2, V_2)	(sp^2, V_3)	18.84*s
(sp^3, V_4)	(sp^2, V_3)	11.17*
(sp^3, V_4)	(p^3, V_3)	(21.06)*s
$N^-(s^2p^4, {}^3P)$	$N(s^2p^3, {}^4S)$	0.04†
(s^2p^4, V_2)	(s^2p^3, V_3)	0.99*
(s^2p^4, V_2)	(sp^4, V_3)	13.52*s
(sp^5, V_2)	(sp^4, V_3)	2.36*
$N(s^2p^3, {}^4S)$	$N^+(s^2p^2, {}^3P_2)$	14.48
(s^2p^3, V_2)	(s^2p^2, V_2)	13.81*
(s^2p^3, V_3)	(sp^3, V_4)	24.77*s
(sp^4, V_3)	(sp^3, V_4)	12.24*
(sp^4, V_3)	(sp^3, V_2)	14.63*
(sp^4, V_3)	(p^4, V_2)	[28.0*]s
$N^-(s^2p^5, V_1)$	$N(s^2p^3, V_2)$	$[-7??]p^2$
$N(s^2p^3, V_3)$	$N^{++}(s^2p, V_1)$	42.62*p^2
$O^-(s^2p^5, {}^2P=V_1)$	$O(s^2p^4, {}^3P_2)$	2.2[a]
(s^2p^5, V_1)	(s^2p^4, V_2)	2.87*
$O(s^2p^4, {}^3P_2)$	$O^+(s^2p^3, {}^4S)$	13.55
(s^2p^4, V_2)	(s^2p^3, V_3)	14.73*
"	(s^2p^3, V_1)	17.17*
"	(sp^4, V_3)	31.76*s
$O^-(s^2p^6, {}^1S=V_0)$	$O(s^2p^4, {}^3P_2)$	$[-6.5]$[aa] p^2
"	(s^2p^4, V_2)	$[-5.8^*]p^2$
$O(s^2p^4, {}^3P_2)$	$O^{++}(s^2p^2, {}^3P_2)$	48.48p^2
(s^2p^4, V_2)	(s^2p^2, V_0)	51.41*p^2
$F^-(s^2p^6, {}^1S=V_0)$	$F(s^2p^5, {}^2P_{1\frac{1}{2}})$	4.13[b]
"	$(s^2p^5, {}^2P=V_1)$	4.15
$F(s^2p^5, {}^2P_{1\frac{1}{2}})$	$F^+(s^2p^4, {}^3P_2)$	17.32[c]
$(s^2p^5, {}^2P=V_1)$	(s^2p^4, V_2)	18.25*
"	(s^2p^4, V_0)	21.17*
$Cl^-(s^2p^6, V_0)$	$Cl(s^2p^5, {}^2P_{1\frac{1}{2}})$	3.75[b]
"	(s^2p^5, V_1)	3.79*
$Cl(s^2p^5, {}^2P_{1\frac{1}{2}})$	$Cl^+(s^2p^4, {}^3P_2)$	12.96
(s^2p^5, V_1)	(s^2p^4, V_2)	13.66*[d]
"	(s^2p^4, V_0)	15.84*[d]
$Br^-(s^2p^6, V_0)$	$Br(s^2p^5, {}^2P_{1\frac{1}{2}})$	3.53[b]
"	(s^2p^5, V_1)	3.68*
$Br(s^2p^5, {}^2P_{1\frac{1}{2}})$	$Br^+(s^2p^4, {}^3P_2)$	11.80
(s^2p^5, V_1)	(s^2p^4, V_2)	12.43*[d]
"	(s^2p^4, V_0)	14.44*[d]
$I^-(s^2p^6, V_0)$	$I(s^2p^5, {}^2P_{1\frac{1}{2}})$	3.22[b]
"	(s^2p^5, V_1)	3.53*
$I(s^2p^5, {}^2P_{1\frac{1}{2}})$	$I^+(s^2p^4, {}^3P_2)$	10.55[c]
(s^2p^5, V_1)	(s^2p^4, V_2)	11.16*[d]
"	(s^2p^4, V_0)	12.93*[d]

Notes for Table IV. † indicates electron affinities taken from a paper by Glockler.[8] These are based on a method of extrapolation similar to one used by Bacher and Goudsmit (private communication), who consider the latter as reliable as any available. They point out, however, that the method implies a power series approximation for ionization energy, which should become less convergent for negative ions (electron affinities). Unfortunately the available accurate electron affinity data are inadequate to serve as a check on the accuracy of the above extrapolation: for H, the extrapolated value agrees closely with the accurate quantum-mechanically calculated value (0.715 volt); for O and F the extrapolated values are about 1 volt lower than the empirical, but the empirical value for O is uncertain, while the data used in the extrapolation are uncertain in both cases. [In the preceding sentence, we are not using Glockler's extrapolated value +3.80 volts for the electron affinity of O, but a value 1.24 volts. Glockler's value is based on the dubious value 18.6 volts for the ionization potential of F, while the value 1.24 is obtained by Glockler's method if the value 17.32 volts estimated by the writer (cf. note *c* below) is used for the ion. pot. of F.] It seems probable that the extrapolated electron affinities of Glockler (except for O and perhaps a few other cases where reliable data were not available) are not in error by amounts greater than ±0.3 to ±1.0 volts.

* indicates *valence state* electron affinities and ionization potentials which have been obtained by combining *ordinary* electron affinities (†, [a], [aa], [b]) or *ordinary* ionization potentials (cf. note *c* below) with valence state energy data given in Table III. In the case of the electron affinities, it should be noted that the data (all given in *brackets* [ ] in Table III) were obtained by simple extrapolations having a similar basis to that used by Glockler for the *ordinary* electron affinities. In case better values for the ordinary electron affinities should be determined in future, the resulting correction needed for the ordinary electron affinity of any given atom in Table III should also be approximately right for all the valence state electron affinities of the same atom.

[a] is based on a fairly reasonable experimental value 2.2±0.2 volts obtained by Lozier by electron impact methods.[9] This is probably preferable to the extrapolated value (cf. bracketed comment in † note above).

[aa] indicates a very rough electron affinity value (150 ±50 kcal.) based on crystal lattice constants.[10]

[b] indicates values based on crystal lattice data, and considered accurate to ±2 percent, given by Mayer and Helmholtz.[11] It should, however, be noted that the value for F may be less accurate, because it involves the heat of dissociation D of F_2; if for instance the accepted value of

[8] G. Glockler, Phys. Rev. **46**, 111 (1934).
[9] W. W. Lozier, Phys. Rev. **46**, 268 (1934).
[10] J. E. Mayer and Maltbie, Zeits. f. Physik **75**, 748 (1932).
[11] J. E. Mayer and L. Helmholtz, Zeits. f. Physik **75**, 19 (1932).

D should be raised, the M. and H. value of the electron affinity of F would be raised by $\frac{1}{2}D$. The accepted value of D is 2.80 ± 0.03 volts, but in the writer's opinion the indicated probable error ±0.03 is far too small, and the value 2.80 itself has no real foundation, although it may happen to be nearly correct. The value 2.80 volts (63.3 ±0.07 kcal.) is based on a determination of the maximum (λ2900) of the ultraviolet continuous absorption of F_2 by von Wartenberg and Taylor, combined with an extrapolation of the interval $\lambda_{conv.}-\lambda_{max}$ as observed in I_2, Br_2 and Cl_2, to F_2 ($\lambda_{conv.}$ = wave-length of convergence of vibrational levels, corresponding to dissociation; not observed in F_2).[12] The extrapolation used (linear variation of $\lambda_e-\lambda_m$ with atomic weight A) has no theoretical basis, and might well be deceptive, since F occupies an exceptional position among the halogens; furthermore, the supposed linear variation of $\lambda_e-\lambda_m$ is actually not even empirically fulfilled for I_2, Br_2, Cl_2 when the most reliable available data on λ_e and λ_m are used (cf. e.g., Mulliken, Phys. Rev. **46**, 549, 1934, Table IIB).

[c] *indicates* for fluorine an estimate of the ionization potential made from data on the s^2p^43p, ^4P, ^2P states of fluorine, using for the $3p$ term value an estimate based on interpolation in the series N, O, Ne, Na; the present estimate of the ionization potential is believed to be much better than Dingle's value 18.6 volts, which is obviously too large. The estimated value 10.55 volts for iodine is based on interpolation and other comparisons between data on other atoms and is believed to be at least as well founded as other estimates in the literature. The ionization potentials given for all other atoms are spectroscopic values (cf. Bacher and Goudsmit).

[d] *indicates* values for Cl^+, Br^+, I^+ which are based on a method of estimation (see Table III) which may give appreciable errors (probably not worse than ±0.5, however). If we may judge by a comparison of F^+, Cl^+, Br^+, I^+ with C, Si, Ge, Sn, the values 2.92, 2.79, 2.69 for $s^2x^2y^2$, V_0 in Table III, and so the ionization potentials $V_1\rightarrow V_0$ in Table IV, are about 0.35 volt too high for Cl^+, Br^+, about 0.4 too low for I^+; but this is uncertain.

[12] H. von Wartenberg, G. Sprenger and J. Taylor, Bodenstein-Festband, p. 61. (Ergänzungsband of the Zeits. f. physik. Chemie, Leipzig, 1931.)

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m_s is parallel to that of any other electron in a similar condition in the same atom is just $\frac{1}{2}$. The quantum-mechanical energy integral taken over a state in which parallel and antiparallel orientations of two m_s's are equally probable is the average of the energy values 0 and $-K$ for the two cases considered separately. Hence $-\frac{1}{2}K(i,j)$ is the correct result. This argument, while perhaps not rigorous, is illuminating.

In Table III the energies of various valence states of a number of atoms and ions are estimated numerically by the use of the energy expressions in Table II taken in connection with available spectroscopic data. In many cases the results obtained can be regarded as only approximate for the well-known reason (among others) that the observed states do not fit Slater's formulas very well. For example, the observed ratio of the intervals $(^1S-{}^1D)/(^1D-{}^3P)$, which should be 3 : 2 for configuration s^2p^2 or s^2p^4 according to Slater's formulas, is actually much nearer 1 : 1. In spite of this difficulty, whose effects have, it is hoped, been minimized by judicious averaging, etc. (cf. Table III), it seems probable that the final results given in Table III should represent fairly good approximations to the desired valence state energies.

In Table IV ionization potentials and electron affinities of a number of atoms are given, for both s and p electrons. Additional values can readily be obtained, when needed, by making use of the excitation energies of valence states, given in Table III. Most of the ionization processes given in Table IV correspond to removal of a valence electron so that if the atom is in state V_n, its positive ion is in state V_{n-1}. Similarly, many of the electron affinities correspond to addition of an electron in such a way as to go from an atom state V_n to a negative ion state V_{n-1}. This type of ionization potentials and electron affinities is what is needed for getting the electronegativity values of Table I. The electron affinities, it should be noted, are not accurate (probable errors ±0.3 up to ±1 volt) except in the case of the halogens: cf. Table IV, note†.

Wave-Mechanical Treatment of the Li_2 Molecule

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A treatment of the Li_2 molecule by the Heitler-London method, with Slater wave functions for the atoms, has been carried out both with and without the customary approximations. In the absence of these approximations the binding computed is only a small fraction of that observed. It is found that the inner shells of the atoms may have an important effect on the magnitude of molecular binding, and may either increase or decrease it. Since their effect is associated with electron exchange it appears that they cannot be replaced by an equivalent potential field without serious error. Triple exchanges of electrons are found to be important, while polar binding is quite negligible in Li_2. A criterion for the applicability of the "interaction operator" is developed; the error involved in its use with Li_2 is small. A variational treatment has also been applied to this molecule. It yielded a binding energy less than that observed by about 0.5 e.v. The elimination of the residual error apparently requires the introduction of the interelectronic distances as coordinates. Convenient methods for the numerical treatment of multiple electron exchanges in complicated molecules are described.

I. INTRODUCTION

IT has not been the purpose of the present investigation to determine with great care the properties of the Li_2 molecule in its normal state, but rather to investigate the potentialities of the Heitler-London method in dealing with such problems, to evaluate in this one case the approximations commonly made in theoretical investigations of molecular binding, to gain insight into the rôle of the inner shells in chemical binding, and to illustrate the application to such problems of a variational method which has already been used in an investigation of H_2 in the normal state.[1]

Only in the treatment of two-electron molecules has it been possible to follow the Heitler-London[2] treatment of H_2 in using approximate molecular wave functions constructed as linear combinations of products of accurate atomic wave functions; in other cases accurate atomic functions are either lacking or of such character that the necessary integrations would be quite difficult. All the available information, not complicated by the introduction of other untested approximations, concerning this fundamental approximation has, therefore, been obtained from treatments of various states of the molecule H_2. The results obtained have been qualitatively correct, so far as experimental checks are available, but quantitatively unsatisfactory, particularly as concerns the normal state of the molecule. The computed binding energies have been decidedly too small, and the computed equilibrium distances too large, it being thus indicated that, as one would expect, for the internuclear distances of interest in such work the Heitler-London approximation is rather poor, and that it becomes constantly worse as the atoms approach each other.

If, instead of accurate atomic wave functions, the approximate ones of Slater[3] are employed it becomes possible to treat in a similar manner molecules which are considerably more complicated. The molecular wave functions set up by the method of Heitler and London may then be expressed as a sum of determinants of the form

$$\begin{vmatrix} f_1(1) & f_2(1) & f_3(1) & \cdots \\ f_1(2) & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ f_1(n) & \cdots & \cdots & f_n(n) \end{vmatrix} \text{(notation henceforth } |f_1(1)\, f_2(2) \cdots f_n(n)|),$$

if there are n electrons in the molecule, each f describing a one-electron orbit of the type used in describing the isolated atoms. The evaluation of the energy associated with such a function appears to have been carried out without approximation only by Gentile,[4] in the consideration of the interaction of an unexcited He atom with another H or He atom; no quantitative experimental checks on his results are available.

[1] James and Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] Heitler and London, Zeits. f. Physik **44**, 455 (1927).
[3] Slater, Phys. Rev. **34**, 1293 (1929).
[4] Gentile, Zeits. f. Physik **63**, 795 (1930).

To facilitate computation two further approximations are customarily made.

First, the inner shells are omitted from consideration, a wave function being set up which involves only the outer electrons, while the effective charge of each nucleus is taken as the algebraic sum of its real charge and the charge of the inner shells. In effect the inner shells are thus treated as consolidated with the nucleus. The energy computed from such a wave function is then compared with the energy of atomic functions similarly constructed, to determine the binding energy of the molecule. Though several arguments for the validity of this process have appeared in the literature they cannot be given much weight, as they deal only with considerations of the interactions of the stripped inner shells, and neglect characteristically quantum-mechanical effects involving the outer shells along with the inner ones. Delbrück,[5] in a treatment of Li_2 in which many approximations were made, has estimated some of the terms in the energy associated with the inner shells. His conclusion that they play no essential rôle in the binding cannot be accepted, however, as he entirely neglected the most important of these terms.

It should be noted that even if it were to be granted that the inner shells are unimportant, the process used for their elimination from the problem would have to be considered to be somewhat arbitrary. For, because of the symmetry of the functions to interchanges of electrons, it is not possible to pass uniquely from a given approximate atomic function to an approximate function describing an electron in a particular state. For instance, the nodeless functions used by Rosen and Ikehara[6] to describe the outer electrons of the alkali metal atoms, could equally logically be replaced by sums of these functions with the similar functions which might be used to represent the inner shell electrons. This change would be accompanied by an arbitrary change in the computed binding energy. Only by explicit inclusion of the inner electrons in the wave function can this ambiguity be eliminated.

The second customary approximation is the use of an "interaction operator," the introduction of which is equivalent to the assumption that the wave functions are accurate solutions of the wave equation for infinite separation of the nuclei. A description of the way in which this may be set up and an analysis of the approximation involved in its use are to be found in the mathematical section of this paper.

The only results which tend to produce confidence in the quantitative value of the H.-L. method have been obtained in treating the normal states of molecules in which the binding is due to a single pair of electrons. Table I gives

TABLE I.

	Dissociation Energy (e.v.)			*Equilibrium Distances (A)*	
	Calc.	Obs.	Obs./Calc.	Calc.	Obs.
H_2[2]	2.87	4.44	1.55	0.87	0.74
Li_2[7]	1.09	1.14	1.05	2.28	2.67
Na_2[6]	0.81	0.76	0.94	2.83	3.08
K_2[6]	0.55	0.51	0.93	4.18	3.91
NaH[8]	2.30	2.56	1.11	1.44	1.6

the results of these computations. Except in the case of H_2 all the approximations mentioned above have been made.

One could desire in the agreement of computation with experiment little more than is obtained in the last four cases. However, the relation of the computed to the observed results for H_2 is very different from that found in those cases where inner shells were omitted from the calculation. It is clear, also, that the similarity which one would expect in this respect if the treatments were essentially similar could be obtained by the inclusion of a repulsion due to the inner shells in those cases where they were omitted. One is thus led to the idea that approximations made in these computations are responsible for their satisfactory outcome, and that they do not form a reasonable basis for the evaluation of the Heitler-London method.

As it does not seem possible to determine either sign or magnitude of the approximations from material in the literature, Li_2 has been

[5] Delbrück, Ann. d. Physik **5**, 36 (1930).
[6] Rosen and Ikehara, Phys. Rev. **43**, 5 (1933).
[7] Bartlett and Furry, Phys. Rev. **38**, 1615 (1931).
[8] Hutchisson and Muskat, Phys. Rev. **40**, 340 (1932).

chosen for such an investigation. The work carried out has been the following:

(1) H.-L. treatment of the molecule, including the inner shells, without computational approximation.

(2) H.-L. treatment of the molecule including the inner shells, using a modified Hamiltonian.

(3) H.-L. treatment without inner shells, using a modified Hamiltonian.[9]

(4) Addition of an ionic term to (1).

(5) Change of the shielding parameters in (2).

By comparison of the various results thus obtained and the experimental value for the dissociation energy, it is possible to determine the value of the H.-L. method in treating such a molecule, justify the use of the modified Hamiltonian, evaluate approximately and analyze the effect of the inner shells on the binding, and estimate the improvement in the energy to be obtained by the methods now usual when the H.-L. method proved to be inadequate. Finally,

(6) A variational treatment has been found to yield considerably more satisfactory results than could be obtained in the above work.

II. Heitler-London and Related Treatments

1. Method

Denoting by $s(n\alpha, i)$ the ith electron in an ns state about nucleus A, with spin α, and by $s'(n\alpha, i)$ that electron in a similar state about nucleus B, the molecular configurations of lowest energy may be designated by

$$1\sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6)$$
$$2\sim s(1\alpha, 1)s'(1\alpha, 2)s'(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s(2\beta, 6)$$
$$3\sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\alpha, 6)$$
$$4\sim s(1\alpha, 1)s'(1\alpha, 2)s(2\beta, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6).$$

To each of these there corresponds a determinant wave function such as

$$\psi_1=(1/C_1)\,|s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6)|,$$

where C_1 is a normalizing factor. The H.-L. functions are constructed as sums of these which make the part of the energy matrix associated with these four functions diagonal.[10] Of these $\psi_1+\psi_2$ describes the basic $^1\Sigma$ state, $\psi_1-\psi_2$, ψ_3 and ψ_4 the lowest $^3\Sigma$ state.

Let

$$U_{mn}=\int \psi_m^*\psi_n dv; \qquad H_{mn}=\int \psi_m^* H\psi_n dv.$$

Here the * denotes the conjugate complex, and may be omitted, since all the wave functions are real. In terms of these quantities the energies associated with the above functions for the singlet and triplet states are $(H_{11}\pm H_{21})/(1\pm U_{21})$, the $+$ being associated with the singlet, the $-$ with the triplet.

The lowest ionic configurations are similarly

$$A\sim s(1\alpha, 1)s'(1\alpha, 2)s(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s(2\beta, 6)$$
$$B\sim s(1\alpha, 1)s'(1\alpha, 2)s'(2\alpha, 3)s(1\beta, 4)s'(1\beta, 5)s'(2\beta, 6)$$

to which there correspond ψ_A and ψ_B, respectively. The linear combinations $\psi_A+\psi_B$ and $\psi_A-\psi_B$ are two zero order singlet ionic functions of the Heitler-London type, the first being symmetric to reflection of the function in the midplane between the nuclei, the second antisymmetric to this transformation. A simple extension of the H.-L. method can now be carried out by making diagonal the part of the energy matrix associated with the six functions $\psi_1+\psi_2$, $\psi_1-\psi_2$, ψ_3, ψ_4, $\psi_A+\psi_B$ and $\psi_A-\psi_B$. As the only non-zero elements off the diagonal are those between the first and fifth functions, the secular equation reduces to four linear equations giving the energies of the other functions and a quadratic equation giving the energies of the proper com-

[9] Essentially the treatment of the problem by Bartlett and Furry.

[10] For a general discussion of this method of obtaining approximate molecular wave functions see Slater, Phys. Rev. **38**, 1109 (1931).

binations of these two functions. The lower root of this equation is the interesting one, yielding for the energy of the basic state a better approximation than that given above in proportion as ionic binding is important in this molecule. Noting equalities between the integrals H_{mn} due to the Hermitian character of the operator H, its symmetry in the electrons and nuclei, and its independence of spin, the secular equation reduces to

$$\begin{vmatrix} (H_{11}+H_{21})-E(U_{11}+U_{21}) & 2H_{1A}-E(2U_{1A}) \\ 2H_{1A}-E(2U_{1A}) & (H_{AA}+H_{BA})-E(U_{AA}+U_{BA}) \end{vmatrix}=0. \quad (1)$$

The normalized one-electron wave functions used in the construction of the molecular wave functions and evaluation of the integrals H_{mn} and U_{mn} were the following:

$$s(1\alpha, 1)=e^{-\delta_1 r_1}\delta(\alpha/\sigma_1)[(2\delta_1)^3/4\pi\cdot 2!]^{\frac{1}{2}},$$

$$s(2\alpha, 1)=r_1 e^{-\delta_2 r_1}\delta(\alpha/\sigma_1)[(2\delta_2)^5/4\pi 4!]^{\frac{1}{2}},$$

$$s'(1\alpha, 1)=e^{-\delta_1 s_1}\delta(\alpha/\sigma_1)[(2\delta_1)^3/4\pi 2!]^{\frac{1}{2}},$$

$$s'(2\alpha, 1)=s_1 e^{-\delta_2 s_1}\delta(\alpha/\sigma_1)[(2\delta_2)^5/4\pi\cdot 4!]^{\frac{1}{2}},$$

where r and s indicate distances from nuclei A and B, respectively, δ_1 and δ_2 are parameters, and σ_1 is the spin coordinate of electron 1. These functions are of the form suggested by Slater;[11] using in them the best possible values of the δ's (in the sense of the Ritz method) one finds for the Li atom an ionization energy of 5.29 e.v., as compared to the experimental 5.37 e.v. The best value for δ_1 is 2.686, and is very nearly independent of the choice of δ_2. The best value of δ_2 is 0.637; the computed energy of the atom is quite insensitive to small changes of this parameter.

Though the ionization energy of the atom computed with these functions is in error by only 0.08 e.v., the error in the total energy is 1.63 e.v. This is principally due to the error in the wave functions for the inner electrons, this error being present also in the computation of the ionic energy and cancelling out on evaluation of the ionization energy as the difference of the two quantities. Similarly it seems probable that though the computed total energy of the molecule may be in error by 3 or 4 e.v. the difference between this and the computed energy of the separated atoms should give a good representation of the binding energy, provided only that the H.-L. method of dealing with the binding electrons is adequate.

If the procedure of Heitler and London were to be followed closely the δ's should be in the ratio $\delta_1/\delta_2=4.21$. In most of the present work, however, this ratio was taken to be 4, both to simplify the numerical work and in view of the following considerations. Wang[12] has shown that in the best wave functions for H_2 of H.-L. form the effective charge of the nuclei is different from that in the separated atoms; Rosen[13] has shown how the value of this parameter varies with the internuclear distance. To obtain the best results possible without an extensive variation of the parameters δ_1 and δ_2 (a prohibitively laborious process in the case of Li_2) it was attempted to estimate what they should be. The effective nuclear charge for the inner shells (i.e., δ_1) was taken as unchanged on formation of the molecule, just as it is essentially unchanged on formation of the atom from the ion. On the other hand, it was assumed that δ_2 would be changed in the same proportion as the δ in the H_2 function, when the internuclear distances are in the same ratio as the distances from the nuclei of the maxima of radial charge density. That is, it was assumed that the essential difference of H_2 and Li_2 in this respect is one of scale. This assumption leads, for an internuclear distance of 3A in Li_2, to $\delta_1/\delta_2=3.96\leqq 4.0$. To prove that no gross error was introduced by such a choice of δ_2 one computation was carried out with $\delta_1/\delta_2=4.25$.

The methods used in the evaluation of the integrals U_{mn} and H_{mn} with the various approximations are described in the mathematical section of this paper.

[11] Slater, Phys. Rev. **36**, 57 (1930).

[12] Wang, Phys. Rev. **31**, 579 (1928).
[13] Rosen, Phys. Rev. **38**, 2099 (1931).

2. Results

In Table II will be found the results of the computations made without further approximations than those implied in the use of the Slater atomic functions in the H.-L. molecular functions. A Morse curve, which should have the general character of the results of such a computation, when fitted to these points has its minimum very near 3.18A, and gives a binding energy, $E-2E_A$, of -0.27 e.v. when $2E_A$, the atomic energies subtracted from the molecular energy, are the best obtainable when using Slater's form of the one-electron functions. Less conservatively one might subtract atomic energies computed with $\delta_1/\delta_2=4$, as in the molecular computation. This increases the binding energy by only 0.04 e.v.; the result is still only a small fraction of the observed binding energy, -1.14 e.v.

TABLE II.

δ_1	δ_2	Internuclear distance R (A)	Energy (atomic units)	$E-2E_A$ (a.u.)	$E-2E_A$ (e.v.)	Δ (e.v.)
2.68	.670	2.78	−29.68815	−.0165	−.223	−.051
2.68	.670	2.98	−29.69069	−.0190	−.257	−.032
2.68	.670	3.18	−29.69130	−.0196	−.265	−.018

Introduction of the modified Hamiltonian changes the energy computed by $2E_A+\Delta$, where E_A is the atomic energy computed with the atomic wave functions appearing in the molecular function and Δ is the error involved in the assumptions leading to the use of this operator. This small quantity is given in the last column of Table II.

Table III gives the computed "interaction energy" (from the modified Hamiltonian) for the treatments of the $^1\Sigma$ state with and without the inner shells included. The result of a similar computation on the repulsive $^3\Sigma$ state is also included.

TABLE III.

State	δ_1	δ_2	R (A)	Interaction Energy (e.v.) With inner shells	Interaction Energy (e.v.) Without	Interaction Energy (e.v.) Difference
$^1\Sigma$	2.68	.670	2.78	−.310	−.992	.682
$^1\Sigma$	2.68	.670	2.98	−.326	−.850	.524
$^1\Sigma$	2.68	.670	3.18	−.327	−.722	.395
$^1\Sigma$	2.68	.632	3.38	−.349	−.681	.332
$^3\Sigma$	2.68	.670	3.18	+.424	+.600	−.176

The introduction of the ionic term into the function was carried out only for $R=2.98$A, the complete energy operator being used. It was found that the best result was obtained by adding three percent of the ionic function, the energy being lowered by only 0.0005 e.v.

3. Discussion

The results summarized in Table II show that a treatment of Li_2, modeled so far as possible after the H.-L. treatment (with the slight modification due to Wang), yields a computed binding energy which resembles but little that deduced from observations. The error, though smaller in magnitude than that found in the work on H_2, is much larger in proportion to the binding energy. Clearly the approximations made by Bartlett and Furry are responsible for their satisfactory results in the treatment of this problem.

The error involved in the use of the approximate Hamiltonian turns out to be small for the distances considered, and changes rapidly (apparently exponentially) with the internuclear distance. The latter of these observations was of course to be expected, as the error has its origin in the overlapping of an approximate atomic function about nucleus A, φ_A, with $(H_B-E_B)\varphi_B$, where φ_B is another atomic function which is a good approximate solution of $(H_B-E_B)\varphi_B=0$ except in the region near nucleus B. (See mathematical section.)

Since this error is small the further discussion can be carried on in terms of the interaction energies, as given in Table III. The effect of using a somewhat different value for δ_2 is indicated by the fourth entry in this table. The smaller value of δ_2 turns out to be the better, but the change to be obtained through such an adjustment is so small that the statements made above need no fundamental modification.

The effect of the inner shells on the computation, on the other hand, is very important. They seem to give rise to a repulsive potential, for the $^1\Sigma$ state, varying much more rapidly with distance than the other terms in the binding energy, and with magnitude ranging between one-half

and three-fourths of the observed binding energies for the various distances. For sufficiently large separations of the atoms this effect would presumably sink to negligibility, but for internuclear distances of the order of the equilibrium distance it is by no means unimportant. Omission of these shells tends to correct for a serious underestimate of the binding energy associated with the external electrons, such as follows from the use of the H.-L. functions, and also shifts the computed equilibrium distance strongly toward smaller values (by 0.9A, in Li_2).

Assuming that the above computations give correct values for the repulsion associated with the inner shells, then the binding energy due to the outer electrons should be about $-1.14-0.80=-1.94$ e.v., for the equilibrium distance. Probably a better estimate would arise from assuming that the computed repulsions are 50 percent too great. (In general the H.-L. method leads to the computation of excessive repulsions as well as insufficient binding.) Then the binding energy computed for the outer electrons should be about -1.7 e.v., of which that found by Bartlett and Furry is 67 percent—a performance closely parallel to that of the same method in the treatment of H_2. The estimated value for the binding due to the $2s$ electrons in Li_2 is thus a little more than a third of that due to the $1s$ electrons in H_2, for the equilibrium distances. However, Delbrück's conclusion that the decrease of the binding in Li_2 with respect to that in H_2 is to be attributed exclusively to the fact that the binding electrons are $2s$ electrons cannot be accepted; the inner shells seem to be effective in this respect both through the repulsion associated with their presence and through the resulting increase in the equilibrium distance, which is apparently of considerable size.

That the inner shells in a molecule do not necessarily exert a repulsive effect is shown by the computation on the $^3\Sigma$ state of Li_2, in which case they produce an attractive potential of about half the magnitude of the repulsive potential in the $^1\Sigma$ state at that distance. This surprising result is due to the fact, now to be demonstrated, that the important terms in the energy associated with the inner shells involve also the outer "binding" electrons, and will thus vary with their nature.

In order to analyze the way in which the inner shells produce their effect it will be necessary to divide the interaction energy into parts which may be thought of as associated with pairs of electrons undergoing transitions of various types in the molecule. It should be emphasized that such a division is a purely formal matter, as indeed is the whole of the discussion which follows. Such observations as can be made have the same sort of significance as the common statement that chemical binding is associated with resonant interchange of the electrons responsible for the binding, and the possibility of such an interpretation is dependent entirely on the choice of wave function for the representation of the molecule. There seems to be sufficient interest associated with the results, however, to justify their presentation.

Now, the interaction energy operator can be separated into parts, all having the same form, associated with each pair of electrons. The interaction energy is similarly divided into parts, each of which consists of an integral involving such a part of the operator, with a weighting factor arising from integrations over the coordinates of the other electrons. These weighting factors would be one or zero if the one-electron functions were all mutually orthogonal; since this is not the case they differ somewhat from these two values. The contributions to the binding energy are conveniently and reasonably grouped according to the nature of the integral which contains the energy operator. A contribution involving an integral such as $\int f_4^*(2)f_3^*(1)\times H_{12}f_2(2)f_1(1)dv_{12}$ may then be thought of as associated with a simultaneous transition of electron 1 from a state described by f_1 to one described by f_3 and of electron 2 from a state described by f_2 to one described by f_4. In Table IV are listed the contributions associated with the possible pairs of transitions, for the computation at $R=2.78$A. In this grouping the numbers and spins of the electrons and the senses of the transitions have been disregarded.

Only the first two terms here do not involve the inner shells. They do not add up to give exactly the result of a computation from which inner shells are excluded, however, the difference being due to a small difference of the normalizing factors $[2+2U_{21}]^{-\frac{1}{2}}$ in the two cases. The other

TABLE IV.

$f_4f_3f_2f_1$	Contribution to the energy (e.v.)
$s(2)s'(2)s(2)s'(2)$	−0.240
$s'(2)s(2)s(2)s'(2)$	−0.828
$s'(2)s(2)s(2)s'(1)$	0.306
$s(2)s(1)s(2)s'(2)$	0.169
$s(1)s(1)s(2)s'(2)$	0.130
$s(1)s(1)s(1)s'(2)$	0.106
$s'(1)s(2)s(2)s'(1)$	0.077
$s(1)s(2)s(1)s'(2)$	−0.029
$s'(1)s(1)s(2)s'(2)$	−0.007
$s(2)s'(1)s(2)s'(2)$	0.004
$s(1)s(2)s(2)s'(2)$	0.002

terms which tend to produce binding are quite unimportant. The larger contributions producing repulsion have the common characteristic of involving at least one electron undergoing a transition between one of the $2s$ states and a $1s$ state about the other nucleus; from the usual point of view this would be taken to mean that the occurrence of electronic rearrangements involving such a transition is responsible for the repulsion. That the substitution of some kind of central field for the inner electrons in a H.-L. computation cannot be a proper simplification is clear, as the possibility of such processes is thus neglected.

One of the largest repulsive contributions of all arises from triple or higher transitions of electrons between different states. Though exceeded in magnitude by only one other contribution these were neglected by Delbrück, who assumed (as is indeed the almost universal practice) that the contributions decrease in magnitude as the number of electron transitions involved increases. Such a criterion is thus proved to be inapplicable, at least when inner shells are present. It will also be noted that three of the five important repulsive terms involve states in at least three of the four electron shells in the molecule. Thus not even by considering the atomic interaction as a sum of interactions of electron shells in pairs can one obtain a satisfactory result; indeed it seems to be exceedingly difficult to suggest any essential simplification in the treatment of such systems which does not introduce a considerable error.

The small improvement produced on introduction of the ionic term (−0.0005 e.v. for $R=2.98$A) is not surprising in the case of the molecule Li_2. This result is, however, to be contrasted with that of Bartlett and Furry, who obtain for this distance a change of −0.05 e.v. in the energy on introduction of this term. Even more surprising is the increasing importance of ionic binding with increasing distance between the atoms which they find. These anomalous results seem to have their origin in the fact that the introduction of the ionic function is essentially a variational process, and can thus be depended upon to give proper results only when all electrons are present and the entire energy operator is used. A similar objection may be made to attempts to improve the H.-L. method by diagonalizing a larger section of the energy matrix, when inner shells are omitted or other approximations are made.[14]

III. VARIATIONAL TREATMENT

1. Method

The quantitatively unsatisfactory outcome of the work described above reveals the necessity of designing an essentially different method for dealing with such systems. The molecule H_2 was chosen as the most suitable subject for the investigation of such a method. The satisfactory outcome of the work on that problem, as described in reference 1, then led to an attempt to extend the method used there to the treatment of the present problem. The most complete generalization, which would consist in the construction of a wave function expressed in terms of the 17 coordinates of which the energy is a function, is clearly impracticable at present. Even the less ambitious project of describing the inner shells of the molecule by Slater functions and the binding electrons by functions of the sort used in treating H_2 proved to be decidedly difficult, because of the nature of the terms involving the distance between these electrons, the r_{12} terms. As a first step in the right direction the work was carried through with the omission of these terms. Then the wave function, like the H.-L. function, was expressible as a sum of products of one-electron functions.

[14] Note, for instance, the excessively strong binding computed for a $^2\Sigma$ state of BeH by Ireland, Phys. Rev. 43, 329 (1933).

$$\psi = \sum_{mnjk} C_{mnjk}[mnjk] = \sum_{mnjk} C_{mnjk} \times \{\psi_{mnjk} + \psi_{nmkj})/[2(6!)]^{\frac{1}{2}}\}, \quad (2)$$

$$\psi_{mnjk} = |s(1\alpha, 1)s'(1\alpha, 2)f(mj\alpha, 3) \times s(1\beta, 4)s'(1\beta, 5)f(nk\beta, 6)|. \quad (3)$$

Here $s(1\alpha, 1)$ and $s'(1\alpha, 1)$ are defined as before, while

$$f(mj\alpha, 1) = e^{-\gamma_2\lambda_1/2}\lambda_1{}^m\mu_1{}^j\delta(\alpha_1, \sigma_1),$$

where $\lambda_1 = (r_1+s_1)/R$, $\mu_1 = (r_1-s_1)/R$, and γ_2 is a parameter independent of m and j. Neither the f's nor the functions ψ_{mnjk} are normalized or orthogonal. This ψ is of the proper character for the description of a singlet state. The desired symmetry of ψ to reflection in the mid-plane is to be obtained by including only those terms $[mnjk]$ for which $j+k$ is even, each ψ_{mnjk} then being symmetric to such a transformation. The adjustment of the constants C_{mnjk} and the determination of the molecular energy were carried out by the methods described in reference 1 and the mathematical section of this paper.

2. Results and discussion

Because of the large amount of numerical work necessary a computation has been made for only one set of values for the parameters. They were chosen to be $\gamma_1 = \delta_1 R = 15$; $\gamma_2 = 4$; $R = 2.98$A, these values giving the greatest numerical convenience available in the desired range of R and γ_2.

When a wave function for the molecule was built up by adding one term at a time, the energy fell rapidly at first on the addition of each new term, but later much more slowly, until in all eighteen terms were introduced. These were all the terms of proper character that could be constructed with mj and nk equal to 00, 01, 02, 10, 11, 12 or 20. The binding energy was then -0.62 e.v., the energy taken for Li being that computed by Wilson.[15] This is to be compared with the -0.20 e.v. computed for this distance by the H.-L. method (the same energy for the separated atoms being used) and the -1.11 e.v. which is indicated by a Morse curve constructed by using experimental values for the molecular constants involved.

[15] Wilson, J. Chem. Phys. **1**, 210 (1933).

The effect of adding new terms to the wave function was somewhat different from that described in the case of H_2, the convergence toward a limit being less definite. Since the value of the secular determinant was rather far from a linear function of λ (the presence of another $^1\Sigma_g$ state in the neighborhood being thus indicated) it would have been rather troublesome to determine exactly the energy associated with each of the preliminary functions used. The average improvement found on adding the last few terms, however, was found to be between 0.02 and 0.03 e.v., as against 0.01 e.v. in the case of H_2. It was thus indicated that the result could be somewhat improved by the addition of more terms of similar character, but since the labor involved in adding each new term to such a complicated function is considerable this has not been done. It may be expected that in the presence of a few r_{12} terms the convergence would be much more satisfactory, and that an excessive number of terms would not be required in the wave function, as such behavior with respect to convergence was found with H_2.

It seems likely that the 0.5 e.v. between the computed and experimental values may be almost entirely due to the absence of the r_{12} terms. A part of this error, though hardly more than a small part, to judge from the results with H_2, might be due to a poor choice of γ_2. Another possibility is that the binding electrons have retained more of their atomic character than is the case in H_2. The binding energy in Li_2 is about 10 percent of the total energy of the outer electrons, against 20 percent in H_2. Associated with the greater ratio of intra-atomic to binding forces there should be a smaller change in the character of the functions as the atoms approach each other. The slow convergence noted might then be associated with a slowly increasing perfection in the expansion of a function of marked atomic character as a sum of an increasing number of terms of molecular character. The remedy for such a situation would be to introduce a term of atomic character—say the Wang function—as a unit in the series. One would thus attempt to expand the difference between the Wang function and the correct one, rather than the entire function, in terms of the two-center functions. Some work of Dr. A. S. Coolidge and

the writer, as yet unpublished, has shown that this scheme is quite ineffective in the treatment of either the normal or lowest $^3\Sigma_u$ state of H_2. It would then seem that no large improvement in the treatment of Li_2 could be expected from such a modification.

Introduction into the wave function of terms depending on the distance between the outer electrons, or something equivalent, would seem to be the next step in this investigation. It is hoped that a satisfactory method for doing this and simultaneously improving the treatment of the inner shells may grow out of an investigation of the Li atom now under way.

IV. Mathematical Section

1. The interaction operator

The use of the interaction operator involves assumptions which do not seem to have been discussed in the literature. Since consideration of these assumptions throws some little light on the range of applicability of this approximation it seems worth while to give them explicit statement. The argument below applies to a nonpolar state of a neutral diatomic molecule. The extension to polar states and polyatomic molecules is simple and obvious, and even charged systems can be treated by a proper modification of the method.

Let the molecule to be considered contain $n=Z_A+Z_B$ electrons, and nuclei with charges Z_A and Z_B, respectively. The wave equation for this molecule is then

$$\left\{\sum_i^n -\nabla_i^2+\frac{2Z_AZ_B}{R}+\sum_{i>j}^{n,\,n-1}\frac{2}{r_{ij}}-\sum_i^n\frac{2Z_A}{r_i}-\sum_i^n\frac{2Z_B}{s_i}-E\right\}\psi=0. \quad (4)$$

Here r_i, s_i and r_{ij} are the distances of electron i from nucleus A, nucleus B and electron j, respectively, and E is the energy of the system in atomic units (13.54 e.v.). Let $\varphi(1, \cdots, n)$ be a single determinant describing a configuration of the molecule (such as $\psi_1(1, \cdots, 6)$ as defined in treating Li_2). φ can be expanded in a well-known manner as a sum of products of subdeterminants, each of which describes a configuration of one of the constituent atoms

$$|f_1(1)f_2(2)\cdots f_n(n)|=|f_1(1)\cdots f_m(m)|\times|f_{m+1}(m+1)\cdots f_n(n)|+\text{similar terms}$$

or

$$\varphi(1, 2, \cdots, n)=\chi_A(1, \cdots m-1, m)\times\chi_B(m+1, m+2, \cdots n)-\chi_A(1, \cdots m-1, m+1)\times\chi_B(m, m+2, \cdots n)+\cdots. \quad (5)$$

The functions f are to be so chosen as to make the determinants χ approximate solutions of atomic equations such as

$$\left\{-\sum_{i=1}^{m=Z_A}\left(\nabla_i^2+\frac{2Z_A}{r_i}\right)+\sum_{i>j}^{m,\,m-1}\frac{2}{r_{ij}}\right\}\chi_A(1, \cdots m)=E\chi_A(1\cdots m) \quad (6)$$

or $H_A\chi_A=E\chi_A$. If χ_A is an exact solution of this equation E will be the correct E for atom A. If this is not the case the root-mean-square error involved in the use of Eq. (6) can be reduced to a minimum by setting E equal, not to this true energy, but to

$$E_A=\int\chi_A^*H_A\chi_Adv\Big/\int\chi_A^2dv. \quad (7)$$

For if

$$(H_A-E_A)\chi_A=\Delta_A, \quad (8)$$

then

$$(H_A-E_A')\chi_A=\Delta_A+(E_A-E_A')\chi_A, \quad (9)$$

and the root-mean-square error in putting $(H_A-E_A')\chi_A=0$ becomes, through the use of (7) and (8),

$$\left\{\int\Delta_A^2dv+(E_A-E_A')^2\int\chi_A^2dv\right\}^{\frac{1}{2}},$$

having its minimum for $E_A'=E_A$. Now

$$H=H_A(1, \cdots m)+H_B(m+1, \cdots n)+H_I(1, \cdots m; m+1, \cdots n), \quad (10)$$

$$H_I(1, \cdots m; m+1, \cdots n)=\sum_{i=1}^{m}\sum_{j=m+1}^{n}h_I(i, j), \quad (11)$$

$$h_I(i, j)=2/R+2/r_{ij}-2/r_j-2/s_i. \quad (12)$$

Then

$$H\chi_A(1, \cdots m)\chi_B(m+1, \cdots n)=(E_A+E_B)\chi_A(1, \cdots m)\chi_B(m+1, \cdots n)+H_I(1, \cdots m; m+1, \cdots n)\chi_A(1, \cdots m)\times\chi_B(m+1, \cdots n)+\Delta_A\chi_B+\chi_A\Delta_B. \quad (13)$$

Using this and a set of similar equations one obtains

$$H\varphi \cong (E_A+E_B)\varphi+\sum_{i\neq j} h_I'(i,j)\varphi, \qquad (14)$$

where $h_I'(i,j)=h_I(i,j)$ when multiplied into any term in φ in which electron i is assigned to a state about nucleus A and j to a state about B, and is zero otherwise. Proceeding as though the approximate equality of Eq. (14) were exact is essentially what one does in using the interaction operator, the error arising from neglect of terms similar to the last two in (13).

This error vanishes if the χ's are accurate atomic functions, as happens only in the case of one-electron atoms, or if $\Delta_A\chi_B$ and $\Delta_B\chi_A$ vanish. In general these products will not vanish unless the Δ's vanish, but it is not difficult to judge when they will be so small as to be safely neglected. When Slater functions are used the χ's will be fairly good solutions of the atomic equation except where the potential energy is very large, near the nucleus or where the electrons are close together. Thus the Δ's will be large in the neighborhood of the inner shells of alkali atoms, but relatively small outside. On the other hand, in the case of the Li^- ion or the atom Be, for instance, Δ will differ from zero appreciably even in the outer shell. Thus one would expect that the neglect of $\Delta_A\chi_B$ in treating a nonpolar configuration of Li_2 would not be serious for fairly large R, because Δ_A is then large only in a restricted region where χ_B is small. Similarly, in treating a polar configuration of this molecule, χ_B for the Li^+ ion will be large in a very restricted region where Δ_A for the Li^-, though it is fairly large in extent, will be rather small in magnitude. The error in this case would thus be expected to be of the order of that found in the nonpolar state. On the other hand, in the treatment of BeH the Δ_A for the Be atom and the χ_B for the H atom will both be extensive, and one may expect serious errors from the neglect of their product. $\Delta_B\chi_A$ in this case of course vanishes because of the vanishing of Δ_B. Since this method of estimating the errors produced in the integrals $\int\varphi_2 H\varphi_1 dv$ takes no account of the nature of the function φ_2 with which the terms $\Delta\chi$ are to be integrated, it might lead one to be unnecessarily conservative in certain cases. One may then supplement the above argument by noticing whether or not φ_2 and $\Delta\chi$ are likely to be large in the same region in phase space.

2. Reduction of the matrix elements

The most characteristic difficulty in the computation of molecular energies is that of expressing the matrix elements, particularly those of energy, in terms of integrals over the coordinates of one or two electrons. This difficulty arises from the fact that the one-electron functions to be used are in large part not mutually orthogonal, the complexity of the expressions for the matrix elements increasing rapidly with the number of such functions involved. The use of non-orthogonal functions is a necessary outcome of the application of the H.-L. method, and is also useful in the treatment of problems of atomic interaction from other points of view. There are two ways in which one may proceed. One is to express the energy matrix element, say, in terms of integrals involving the non-orthogonal functions, so collecting terms as to obtain a sum of integrals containing parts of the Hamiltonian operator, with factors which are complicated functions of integrals over the coordinates of single electrons. The other is to obtain a simple expression for the matrix elements in terms of orthogonalized combinations of the original functions, and to construct the integrals involving the orthogonalized functions as linear combinations of the integrals involving the original functions. The first of these processes is more advantageous the more complex the system and the fewer the electronic configurations to be considered, being especially suited for work by any simple modification of the H.-L. method. After developing this process as it was applied to the treatment of Li_2 by the H.-L. method, the second process will be illustrated by explicit application to the variational treatment of this problem, for which it is preferable.

The first step in the evaluation of the integral $\int\varphi_2^* H\varphi_1 dv$, where

$$\varphi_1=|f_1(1)f_2(2)\cdots f_n(n)|,$$
$$\varphi_2=|f_1'(1)f_2'(2)\cdots f_n'(n)| \qquad (15)$$

and $f_1\cdots f_n$ and $f_1'\cdots f_n'$ are sets of n linearly independent functions, is to express φ_1 and φ_2

in terms of $F_1 \cdots F_n$ and $F_1' \cdots F_n'$. Here the F's shall be normalized linear combinations of the f's and the F''s normalized linear combinations of the f''s such that F_i is orthogonal to all F''s, except, possibly, F_i'. By a familiar property of determinants

$$\varphi_1 = |g_1(1) \cdots g_n(n)|, \tag{16}$$

if

$$g_i = a_{i1}f_1 + a_{i2}f_2 + \cdots + a_{in}f_n, \quad a_{ii} = 1. \tag{17}$$

Now the constants a_{ij} may be so chosen as to produce those orthogonality relations between the g's and g''s which one wishes to hold between the F's and F''s. In the present work this could be done, for instance, by making the g's and g''s mutually orthogonal among themselves, with $g_i = g_i'$ whenever possible; it is to such a situation that the discussion which follows particularly applies. After dividing the f's into groups with respect to spin, angular momentum about the internuclear axis, etc., such that every function in a group is orthogonal to all functions not in that group, orthogonal linear combinations of the members of each group can be made. Simple ways of doing this, depending on the symmetry properties of the system, are often available. In any case one can use the standard process, as described in Courant and Hilbert's "Methoden der Mathematischen Physik I," p. 34. From the g's one then obtains the desired F's by normalization.

$$F_i = N_i g_i, \tag{18}$$

where

$$N_i = \left\{ \sum_j \sum_k a_{ij} a_{ik} \int f_j^*(1) f_k(1) dv_1 \right\}^{-\frac{1}{2}}. \tag{19}$$

Then

$$\varphi_1 = (1/N_1 N_2 \cdots N_n) |F_1(1) \cdots F_n(n)|, \tag{20}$$

and

$$\int \varphi_1^2 dv = n!/(N_1 N_2 \cdots N_n)^2, \tag{21}$$

because of the orthogonality and normalization of the F's.

Now, because of the symmetry of H to any interchange of electrons,

$$\int |F_i'|^* H |F_i| dv = n! \int |F_i'|^* H \{F_1(1) F_2(2) \cdots F_n(n)\} dv, \tag{22}$$

each term in the determinant $|F_i|$, when operated on by H, multiplied by $|F_i'|$ and integrated over all space giving the same result. Hence, using (21) one obtains

$$E_{12} = \int \varphi_2^* H \varphi_1 dv \Big/ \left(\int \varphi_2^* \varphi_2 dv \int \varphi_1^* \varphi_1 dv \right)^{-\frac{1}{2}} = \int |F_i'|^* H F_1(1) \cdots F_n(n) dv. \tag{23}$$

It is in the evaluation of this quantity (the integral $\int \varphi_2^* H \varphi_1 dv$ with φ_1 and φ_2 separately normalized to 1) that we shall be interested.

Because of the symmetry of H in its arguments and the fact that no part of it involves the coordinates of more than two electrons one can write

$$H = \sum_{i>j} h_{ij}. \tag{24}$$

For a neutral diatomic molecule, for instance,

$$h_{ij} = -\frac{1}{Z_A + Z_B - 1} \left(\nabla_i^2 + \nabla_j^2 + \frac{2Z_A}{r_i} + \frac{2Z_B}{s_i} + \frac{2Z_A}{r_j} + \frac{2Z_B}{s_j} \right) + \frac{2}{r_{ij}}. \tag{25}$$

Introducing this into (23), expanding the determinant and noting the orthogonality relations one finds

$$E_{12} = \sum_{i>j} S_{ij} \left(\int F_i'^*(i) F_j'^*(j) h_{ij} F_i(i) F_j(j) dv_{ij} - \int F_i'^*(j) F_j'^*(i) h_{ij} F_i(i) F_j(j) dv_{ij} \right), \tag{26}$$

where

$$S_i=\int F_i'^*(1)F_i(1)dv_1, \qquad S_{ij}=S/S_iS_j, \qquad S=\prod_i^n S_i. \tag{27}$$

Remembering that the matrix transforming the f's into the F's is

$$\|N_ia_{ij}\|=\|c_{ij}\|, \tag{28}$$

one can get out of (26) K_{pqrs}, the coefficient in E_{12} of the integral $\int f_r'^*(x)f_s'^*(y)h_{xy}f_p(x)f_q(y)dv_{xy}$, where the arguments no longer refer to definite electrons. This is readily seen to be

$$K_{pqrs}=\sum_{i\neq j} S_{ij}(c_{ip}c_{jq}c_{ir}'c_{js}'-c_{ip}c_{jq}c_{is}'c_{jr}')=S\sum_{i\neq j}(d_{ip}d_{jq}d_{ir}'d_{js}'-d_{ip}d_{jq}d_{is}'d_{jr}'), \tag{29}$$

if

$$d_{ip}=c_{ip}S_i^{-\frac{1}{2}}, \tag{30}$$

it being assumed that none of the S_i's vanish. (If one should vanish the energy expression is greatly simplified and the work can be started on a different basis.) Observing that (29) may be written

$$K_{pqrs}=S\{\sum_i d_{ip}d_{ir}'\sum_j d_{jq}d_{js}'-\sum_i d_{ip}d_{is}'\sum_j d_{jq}d_{jr}'\},$$

one obtains finally

$$K_{pqrs}=S\{D_{pr}D_{qs}-D_{qr}D_{ps}\}, \tag{31}$$

where

$$D_{ps}=\sum_i d_{ip}d_{is}'. \tag{32}$$

Thus $\|D_{ij}\|$ is the matrix formed by postmultiplying the conjugate of the matrix $\|d_{ij}\|$ by the matrix $\|d_{ij}'\|$. Having constructed the matrix $\|D_{ij}\|$ it is a simple matter to find the coefficient of any integral in the energy matrix element; summing over the contributions from each possible integral E_{12} is then found.

To summarize the process: Determine the matrices of real constants $\|c_{ij}\|$, $\|c_{ij}'\|$ which convert the functions f, f' into the normalized and properly orthogonalized functions F, F'. Divide the ith row of each matrix by $S_i^{\frac{1}{2}}$, and postmultiply the conjugate of the first matrix by the second. From the matrix $\|D_{ij}\|$ resulting the coefficients K_{pqrs} can then be obtained using (31).

To compute E_{12}', the interaction energy matrix element, one need only substitute the integrals $\int f_r^*(x)f_s^*(y)[h_1'(x,y)+h_1'(y,x)]f_p(x)\times f_q(y)d_{xy}$ for the integrals $\int f_r^*(x)f_s^*(y)h_{xy}f_p(x)\times f_q(y)d_{xy}$, the coefficients K_{pqrs} being computed as before.

The second method mentioned above of assembling the simple integrals into matrix elements, which will now be illustrated, is particularly useful when many electronic configurations of a system are to be considered, or a linear function of many parameters is to be used in a variational attack on the problem. One advantage lies in the fact that in the computation of extensive tables of integrals involving orthogonalized functions it is possible to construct tables of intermediate quantities which enter many of the matrix elements. A corresponding reduction in the labor of computing many sets of the coefficients K_{pqrs}, on the other hand, does not appear to be attainable. It is also possible to make immediate use of material arranged in this way for the treatment of one problem, say the normal state of Li_2, in the treatment of other problems—states of the same molecule with different symmetry characteristics, or states of related ionic molecules, as Li_2^+.

The first problem to be considered is that of expressing $\int \psi^*_{m_2n_2j_2k_2}\psi_{m_1n_1j_1k_1}dv$ and $\int \psi^*_{m_2n_2j_2k_2}\times H\psi_{m_1n_1j_1k_1}dv$ with good approximation in terms of a few integrals involving orthogonalized one-electron functions, in such a way as to make maximum use of the relations between the various matrix elements. The orthogonalized functions to be used in place of $s(1\alpha,1)$, $f(mj\alpha,1)$, etc., are

$$\begin{aligned} S(1\alpha,1)&=s(1\alpha,1),\\ S'(1\alpha,1)&=s'(1\alpha,1)-J_1s(1\alpha,1),\\ F(mj\alpha,1)&=f(mj\alpha,1)+t(mj)s(1\alpha,1)\\ &\quad +t'(mj)s'(1\alpha,1). \end{aligned} \tag{33}$$

It is most convenient to make $t(mj)=(-1)^j\times t'(mj)$, so that $F(mj\alpha,1)$ and $f(mj\alpha,1)$ will have the same definite symmetry to reflection in the plane bisecting the internuclear axis.

Let $J_1=\int s(1,1)s'(1,1)dv_1$,

$J_5=\int S'^2(1,1)dv_1=1-J_1^2$,

$J_{mj}=\int f(mj,1)s(1,1)dv_1$,

$J_{mj}'=\int f(mj,1)s'(1,1)dv_1=(-1)^jJ_{mj}$,

$J_{mj,nk}=\int f(mj,1)f(nk,1)dv_1$, (34)

$J_{MJ,NK}=\int F(mj,1)F(nk,1)dv_1$.

Then $t_{mj}=(-1)^jt_{mj}'=-(J_{mj}-J_1J_{mj}')/J_5$, (35)

$$J_{MJ,\,NK}=\delta((-1)^{j+k},1)\{J_{mj,\,nk}-(1/J_5)(J_{mj}J_{nk}+J_{mj}'J_{nk}'-J_1[J_{mj}J_{nk}'+J_{mj}'J_{nk}])\}. \quad (36)$$

Expressing the ψ's in terms of orthogonalized functions according to (16) and (17), and transforming the integral as in (22), one obtains immediately

$$(1/6!)\int \psi^*_{m_2n_2j_2k_2}\psi_{m_1n_1j_1k_1}dv=J_5^2J_{M_1J_1,\,M_2J_2}J_{N_1K_1,\,N_2K_2}. \quad (37)$$

Similarly

$$(1/6!)\int \psi^*_{m_2n_2j_2k_2}H\psi_{m_1n_1j_1k_1}dv=\int \psi^*_{m_2n_2j_2k_2}HS(1\alpha,1)S'(1\alpha,2)F(m_1j_1\alpha,3)$$
$$\times S(1\beta,4)S'(1\beta,5)F(n_1k_1\beta,6)dv. \quad (38)$$

Now, let

$$H=H_1+H_2+H_3+H_4. \quad (39)$$

H_1 shall contain those terms in H which refer only to electrons 1, 2, 4 and 5, plus the repulsion of the nuclei. H_2 shall contain those terms in the operator which involve only electrons 3 and 6, except for $2/r_{36}$, which shall be H_3. H_4 shall contain all other parts of the operator, these being electron interaction terms involving one electron in an inner and one in an outer shell. The energy integrals E_i associated with the operators H_i will be dealt with separately.

Carrying out the integrations over the coordinates of electrons 3 and 6 one obtains

$$(1/6!)\int \psi^*_{m_2n_2j_2k_2}H_1\psi_{m_1n_1j_1k_1}dv=J_{M_1J_1,\,M_2J_2}J_{N_1K_1,\,N_2K_2}\int |S(1\alpha,1)S'(1\alpha,2)S(1\beta,4)S'(1\beta,5)|^*$$
$$\times H_1S(1\alpha,1)S'(1\alpha,2)S(1\beta,4)S'(1\beta,5)dv_{1245}. \quad (40)$$

Now, the integral which appears here is just J_5^2 times the energy of Li_2^{++}, as computed by the H.-L. method. That energy differs from the energy of the separated inner shells, E_s, plus the electrostatic repulsion energy of the ions, $2/R$, by terms of the order of J_1^2, which is about 10^{-9} for the values of R which are of interest. With negligible error, then, one can write

$$E_1=J_{M_1J_1,\,M_2J_2}J_{N_1K_1,\,N_2K_2}(2/R+E_s). \quad (41)$$

Proceeding similarly one finds to a similar approximation

$$E_2=J_{M_1J_1,\,M_2J_2}V_{N_1K_1,\,N_2K_2}+J_{N_1K_1,\,N_2K_2}V_{M_1J_1,\,M_2J_2}, \quad (42)$$

where

$$V_{M_1J_1,\,M_2J_2}=\int F^*(m_2j_2,1)(-\nabla_1^2-6/r_1-6/s_1)F(m_1j_1,1)dv_1. \quad (43)$$

$V_{M_1J_1,\,M_2J_2}$ can be considered as a matrix component of the energy of one of the outer electrons, the mutual energy with other electrons being excluded. Likewise one obtains

$$E_3=\int F(m_2j_2,3)F(n_2k_2,6)(2/r_{36})F(m_1j_1,3)F(n_1k_1,6)dv_{12}, \quad (44)$$

a matrix component of the mutual energy of the outer electrons. Finally, defining

$$X_{M_1J_1,\,M_2J_2}=V_{M_1J_1,\,M_2J_2}+\delta((-1)^{j_1+j_2},\,1)\Big\{8\int S^2(1,\,1)(1/r_{12})F(m_1j_1,2)F(m_2j_2,\,2)dv_{12}$$
$$-4\int S(1,\,1)F(m_1j_1,\,1)(1/r_{12})S(1,\,2)F(m_2j_2,\,2)dv_{12}\Big\},\quad(45)$$

a matrix element of the energy of an outer electron, exclusive of the interaction with the other outer electron, one obtains

$$E_4=J_{N_1K_1,\,N_2K_2}\{X_{M_1J_1,\,M_2J_2}-V_{M_1J_1,\,M_2J_2}\}+J_{M_1J_1,\,M_2J_2}\{X_{N_1K_1,\,N_2K_2}-V_{N_1K_1,\,N_2K_2}\}.\quad(46)$$

Thus

$$(1/6!)\int\psi^*_{m_2n_2j_2k_2}H\psi_{m_1n_1j_1k_1}dv=J_{M_1J_1,\,M_2J_2}J_{N_1K_1,\,N_2K_2}(2/R+E_s)+J_{M_1J_1,\,M_2J_2}X_{N_1K_1,\,N_2K_2}$$
$$+J_{N_1K_1,\,N_2K_2}X_{M_1J_1,\,M_2J_2}+2\int F(m_2j_2,\,1)F(n_2k_2,\,2)(1/r_{12})F(m_1j_1,\,1)F(n_1k_1,\,2)dv_{12},\quad(47)$$

terms of the order of J_1^2 being neglected throughout.

Only the last integral in (47) is characteristic of the particular matrix element to be computed, the other quantities entering an extensive treatment of the system many times. Since $(2/R+E_s)$ enters each of the matrix elements with the corresponding element of the unity matrix as factor, the last three terms of (47) give the "matrix element of $H-2/R-E_s$." It is helpful in the computation to solve the secular equation for this more convenient quantity. This separation of the inner shell energy is essentially different from that which is usually carried out, as the exchange terms have been preserved, many of them having been lumped together into integrals in which, formally, only functions of the outer electrons appear. This again illustrates the purely formal character of the "exchange terms"; even those which appear in this work could be made to disappear by proper modification of the wave functions.

The computation of the X's is similar to, but simpler than that of the last integral in (47). That integral is a sum of 81 integrals involving the unorthogonalized functions. It is conveniently computed by the obvious 9-term formula from tables of intermediate functions, some of which appear elsewhere in the work. These are the integrals

$$\int s^2(1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$
$$\int s(1,\,1)s'(1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$
$$\int s(1,\,1)f(n_1k_1,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12}$$

and

$$\int f(n_1k_1,\,1)f(n_2k_2,\,1)(1/r_{12})F(m_1j_1,\,2)F(m_2j_2,\,2)dv_{12},$$

each of which can be computed from integrals involving the original functions by a nine term formula.

3. Evaluation of integrals

The integrals encountered in this work can be evaluated as functions of the following simpler quantities.

$$A_n(\sigma,\,\gamma)=\int_\sigma^\infty\lambda^ne^{-\gamma\lambda}d\lambda,\qquad R_\tau^{\,n}=\int_{-1}^{+1}P_\tau(\mu)\mu^nd\mu,$$

$$B_n(\gamma)=\int_{-1}^{+1}\mu^n e^{-\gamma\mu}d\mu, \qquad G_\tau{}^n(\gamma)=\int_{-1}^{+1}e^{-\gamma\mu}P_\tau(\mu)\mu^n d\mu,$$

$$H_\tau(m,\gamma_1,n,\gamma_2)=\int_1^\infty d\lambda_1\int_1^\infty d\lambda_2 Q_\tau\binom{\lambda_1}{\lambda_2}P_\tau\binom{\lambda_2}{\lambda_1}\lambda_1{}^m\lambda_2{}^n e^{-(\gamma_1\lambda_1+\gamma_2\lambda_2)} \qquad \begin{matrix}\lambda_1>\lambda_2\\ \lambda_2>\lambda_1\end{matrix}.$$

Here P_τ and Q_τ are the Legendre functions of the first and second kind, respectively. Rosen[16] has discussed the integrals A, B, R and G, while Rosen[13] and James and Coolidge[1] give formulas for $H_\tau(m,\gamma_1,n,\gamma_2)$ when $\gamma_1=\gamma_2$. The following generalizations of their formulas enable one to deal with the case of $\gamma_1\neq\gamma_2$.

$$H_0(m,\gamma_1,n,\gamma_2)=F_m(\gamma_1)A_n(\gamma_2)+F_n(\gamma_2)A_m(\gamma_1)-T(m,\gamma_1,n,\gamma_2)-T(n,\gamma_2,m,\gamma_1), \tag{48}$$

$$\begin{aligned}H_\tau(m,\gamma_1,n,\gamma_2)=(1/\tau^2)[&(2\tau-1)^2H_{\tau-1}(m+1,\gamma_1,n+1,\gamma_2)+(\tau-1)^2H_{\tau-2}(m,\gamma_1,n,\gamma_2)\\
&-(2\tau-1)(2\tau-3)\{H_{\tau-2}(m+2,\gamma_1,n,\gamma_2)+H_{\tau-2}(m,\gamma_1,n+2,\gamma_2)\}\\
&+2(2\tau-1)(2\tau-5)H_{\tau-3}(m+1,\gamma_1,n+1,\gamma_2)\\
&-(2\tau-1)(2\tau-7)\{H_{\tau-4}(m+2,\gamma_1,n,\gamma_2)+H_{\tau-4}(m,\gamma_1,n+2,\gamma_2)\\
&+2(2\tau-1)(2\tau-9)H_{\tau-5}(m+1,\gamma_1,n+1,\gamma_2)-\cdots,\end{aligned} \tag{49}$$

until for even τ $\quad -(2\tau-1)\{H_0(m+2,\gamma_1,n,\gamma_2)+H_0(m,\gamma_1,n+2,\gamma_2)-S(m+1,\gamma_1,n,\gamma_2)$
$\qquad -S(n+1,\gamma_2,m,\gamma_1)\}]$,

for odd τ $\quad +(2\tau-1)\{2H_0(m+1,\gamma_1,n+1,\gamma_2)-S(m,\gamma_1,n+1,\gamma_2)-S(n,\gamma_2,m+1,\gamma_1)\}$.

The auxiliary quantities appearing in these formulas can all be computed by means of recurrence relations.

$$T(m,\gamma_1,n,\gamma_2)=\int_1^\infty\lambda_1{}^m e^{-\gamma_1\lambda_1}Q_0(\lambda_1)d\lambda_1\int_{\lambda_1}^\infty\lambda_2{}^n e^{-\gamma_2\lambda_2}d\lambda_2,$$

$$T(m,\gamma_1,n,\gamma_2)=(1/\gamma_2)[nT(m,\gamma_1,n-1,\gamma_2)+F_{m+n}(\gamma_1+\gamma_2)], \tag{50}$$

$$T(m,\gamma_1,0,\gamma_2)=F_m(\gamma_1+\gamma_2)/\gamma_2, \tag{51}$$

$$F_n(\gamma)=\int_1^\infty\lambda^n e^{-\gamma\lambda}Q_0(\lambda)d\lambda,$$

$$F_n(\gamma)=F_{n-2}(\gamma)+(1/\gamma)[nF_{n-1}(\gamma)-(n-2)F_{n-3}(\gamma)-A_{n-2}(\gamma)], \tag{52}$$

$$F_0(\gamma)=\tfrac{1}{2}[(\ln 2\gamma+C)(e^{-\gamma}/\gamma)-E_i(-2\gamma)(e^{\gamma}/\gamma)], \tag{53}$$

$$F_1(\gamma)=\tfrac{1}{2}[(\ln 2\gamma+C)e^{-\gamma}(1/\gamma+1/\gamma^2)-E_i(-2\gamma)e^{\gamma}(-1/\gamma+1/\gamma^2)], \tag{54}$$

$$S(m,\gamma_1,n,\gamma_2)=\int_1^\infty\lambda_1{}^m e^{-\gamma_1\lambda_1}d\lambda_1\int_1^{\lambda_1}\lambda_2{}^n e^{-\gamma_2\lambda_2}d\lambda_2,$$

$$\begin{aligned}S(m,\gamma_1,n,\gamma_2)&=(1/\gamma_1)[mS(m-1,\gamma_1,n,\gamma_2)+A_{m+n}(\gamma_1+\gamma_2)]\\
&=A_0(\gamma_2)A_m(\gamma_1)+(1/\gamma_2)[nS(m,\gamma_1,n-1,\gamma_2)-A_{m+n}(\gamma_1+\gamma_2)],\end{aligned} \tag{55}$$

$$S(0,\gamma_1,m,\gamma_2)=(1/\gamma_1)A_m(\gamma_1+\gamma_2), \tag{56}$$

$$S(m,\gamma_1,0,\gamma_2)=A_0(\gamma_2)A_m(\gamma_1)-(1/\gamma_2)A_m(\gamma_1+\gamma_2), \tag{57}$$

$$S(m,\gamma_1,n,\gamma_2)+S(n,\gamma_2,m,\gamma_1)=A_m(\gamma_1)A_n(\gamma_2). \tag{58}$$

[16] Rosen, Phys. Rev. **38**, 255 (1931).

All the required integrals except those involving $1/r_{ij}$ are easily evaluated in terms of the functions A_n and B_n, by expressing the integrand in polar or elliptic coordinates, according to the nature of the one-electron functions involved. The more troublesome integrals $\int f_1(i)(1/r_{ij})f_2(j)dv_{ij}$ fall into two groups. If f_1, say, is simply expressible in terms of polar coordinates about one of the nuclei one may determine the potential due to this distribution.[17]. Multiplying by f_2 and integrating in polar or elliptic coordinates, as may be necessary, these integrals are also found in terms of A's and B's. If neither f_1 nor f_2 has a simple potential it is usually desirable to make use of Neumann's expansion of $1/r_{12}$ in elliptic coordinates.

$$\frac{1}{r_{12}}=\frac{2}{R}\sum_{\tau=0}^{\infty}\sum_{\nu=0}^{\infty}D_\tau^\nu P_\tau^\nu\begin{pmatrix}\lambda_2\\ \lambda_1\end{pmatrix}Q_\tau^\nu\begin{pmatrix}\lambda_1\\ \lambda_2\end{pmatrix}P_\tau^\nu(\mu_1)P_\tau^\nu(\mu_2)\cos\nu(\varphi_1-\varphi_2)\qquad\begin{matrix}\lambda_1>\lambda_2\\ \lambda_2>\lambda_1\end{matrix},$$

$$D_\tau^0=2\tau+1,\qquad D_\tau^\nu=(-1)^\nu 2(2\tau+1)[(\tau-\nu)!/(\tau+\nu)!]^2,\qquad \text{for } \nu>0.$$

Integration of f_1 and f_2 with each term of the series gives a quantity expressible in terms of functions defined above. The higher terms of the resulting series often vanish identically, but this does not happen when, for instance, exponential factors in μ appear in both f_1 and f_2. The convergence with increasing τ of the infinite series has in the cases met in this investigation been adequate, though in one case an inconvenient number of terms had to be computed.

The integrals required in the work with H.-L. type functions are not reproduced here; some of them are to be found elsewhere in the literature.[5, 7, 8] The integrals entering the variational treatment of the problem follow. Arguments are omitted where no confusion will result.

$$\gamma_1=R\delta_1;\qquad \kappa=(\gamma_1+\gamma_2)/2.$$

$$J_{mj}=(\pi\delta_1^3)^{\frac{1}{2}}(R^3/4)\{A_{m+2}(\kappa)B_j(\gamma_1/2)-A_m(\kappa)B_{j+2}(\gamma_1/2)\},$$

$$J_{mj,\,nk}=\delta((-1)^{j+k},1)\frac{\pi R^3}{2}\left\{\frac{A_{m+n+2}(\gamma_2)}{j+k+1}-\frac{A_{m+n}(\gamma_2)}{j+k+3}\right\},$$

$$\int s(1,1)f(mj,1)(1/r_1)dv_1=(\pi\delta_1^3)^{\frac{1}{2}}(R^2/2)\{A_{m+1}(\kappa)B_j(\gamma_1/2)-A_m(\kappa)B_{j+1}(\gamma_1/2)\},$$

$$\int s'(1,1)f(mj,1)(1/r_1)dv_1=(\pi\delta_1^3)^{\frac{1}{2}}(R^2/2)\{A_{m+1}(\kappa)B_j(-\gamma_1/2)-A_m(\kappa)B_{j+1}(-\gamma_1/2)\},$$

$$\int f(mj,1)f(nk,1)(1/r_1)dv_1=\pi R^2\left\{\frac{A_{m+n+1}(\gamma_2)}{j+k+1}\delta((-1)^{j+k},1)-\frac{A_{m+n}(\gamma_2)}{j+k+2}\delta((-1)^{j+k},-1)\right\},$$

$$\int f(mj,1)\nabla_1^2 s(1,1)dv_1=\delta_1^2 J_{mj}-R\gamma_1(\pi\delta_1^3)^{\frac{1}{2}}\{A_{m+1}(\kappa)B_j(\gamma_1/2)-A_m(\kappa)B_{j+1}(\gamma_1/2)\},$$

$$\begin{aligned}\int f(mj,1)\nabla_1^2 f(nk,1)dv_1=2\pi R\{&[k(k-1)/(j+k-1)]A_{m+n}(\gamma_2)+[1/(j+k+1)]\\ &\times[-n(n-1)A_{m+n-2}(\gamma_2)+n\gamma_2 A_{m+n-1}(\gamma_2)+(n(n+1)-k(k+1)-(\gamma_2/2)^2)A_{m+n}(\gamma_2)\\ &-(n+1)\gamma_2 A_{m+n+1}(\gamma_2)+(\gamma_2/2)^2 A_{m+n+2}(\gamma_2)]\}\delta((-1)^{j+k},1),\end{aligned}$$

$$\begin{aligned}\int s^2(1,1)(1/r_{12})s(1,2)f(mj,2)dv_{12}&\\ =\int s(1,1)f(mj,1)(1/r_1)dv_1-(\pi\delta_1^3)^{\frac{1}{4}}(R^2/2)\{&(\gamma_1/2)(A_{m+2}(\gamma_1+\kappa)B_j(3\gamma_1/2)-A_mB_{j+2})\\ &+A_{m+1}B_j-A_mB_{j+1}\},\end{aligned}$$

[17] Jeans, *Electricity and Magnetism*, Fifth Edition, p. 224.

$$\int s^2(1,1)(1/r_{12})s'(1,2)f(mj,2)dv_{12}$$
$$=\int s'(1,1)f(mj,1)(1/r_1)dv_1-(\pi\delta_1{}^3)^{\frac{1}{2}}(R^2/2)\{(\gamma_1/2)(A_{m+2}(\gamma_1+\kappa)B_j(\gamma_1/2)-A_mB_{j+2})$$
$$+A_{m+1}B_j-A_mB_{j+1}\},$$

$$\int s(1,1)s'(1,1)(1/r_{12})s(1,2)f(mj,2)dv_{12}$$
$$=(\pi\delta_1{}^3)^{\frac{1}{2}}(\gamma_1{}^3R^2/8)\{R_0{}^0G_0{}^j(\gamma_1/2)H_0(2,\gamma_1,m+2,\kappa)-R_0{}^0G_0{}^{j+2}H_0(2,m)-R_0{}^2G_0{}^jH_0(0,m+2)$$
$$+R_0{}^2G_0{}^{j+2}H_0(0,m)-5R_2{}^2G_2{}^jH_2(0,m+2)+5R_2{}^2G_2{}^{j+2}H_2(0,m)\},$$

$$\int s^2(1,1)(1/r_{12})f(mj,2)f(nk,2)dv_{12}$$
$$=\int f(mj,1)f(nk,1)(1/r_1)dv_1-(\pi R^2/2)\{(\gamma_1/2)(A_{m+n+2}(2\kappa)B_{j+k}(\gamma_1)-A_{m+n}B_{j+k+2})$$
$$+A_{m+n+1}B_{j+k}-A_{m+n}B_{j+k+1}\},$$

$$\int s(1,1)s'(1,1)(1/r_{12})f(mj,2)f(nk,2)dv_{12}$$
$$=(\pi R^2\gamma_1{}^3/8)\{R_0{}^0R_0{}^{j+k}H_0(2,\gamma_1,m+n+2,\gamma_2)-R_0{}^2R_0{}^{j+k}H_0(0,m+n+2)$$
$$-R_0{}^0R_0{}^{j+k+2}H_0(2,m+n)+R_0{}^2R_0{}^{j+k+2}H_0(0,m+n)-5R_2{}^2R_2{}^{j+k}H_2(0,m+n+2)$$
$$+5R_2{}^2R_2{}^{j+k+2}H_2(0,m+n)\},$$

$$\int s(1,1)f(mj,1)(1/r_{12})\begin{pmatrix}s(1,2)\\ s'(1,2)\end{pmatrix}f(nk,2)dv_{12}$$
$$=\frac{\pi R^2\gamma_1{}^3}{8}\sum_{\tau=0}^{\infty}\begin{pmatrix}1\\ (-1)^{k+\tau}\end{pmatrix}(2\tau+1)\{G_\tau{}^j(\gamma_1/2)G_\tau{}^k(\gamma_1/2)H_\tau(m+2,\kappa,n+2,\kappa)$$
$$-G_\tau{}^jG_\tau{}^{k+2}H_\tau(m+2,n)-G_\tau{}^{j+2}G_\tau{}^kH_\tau(m,n+2)+G_\tau{}^{j+2}G_\tau{}^{k+2}H_\tau(m,n)\},$$

$$\int s(1,1)f(m_1j_1,1)(1/r_{12})f(m_2j_2,2)f(n_2k_2,2)dv_{12}$$
$$=\frac{(\pi\delta_1)^{\frac{1}{2}}R^5}{8}\sum_{\tau=0}^{j_2+k_2+2}(2\tau+1)\{G_\tau{}^j(\gamma_1/2)R_\tau{}^{j_2+k_2}H_\tau(m_1+2,\kappa,m_2+n_2+2,\gamma_2)-G_\tau{}^{j_1}R_\tau{}^{j_2+k_2+2}$$
$$\times H_\tau(m_1+2,m_2+n_2)-G_\tau{}^{j_1+2}R_\tau{}^{j_2+k_2}H_\tau(m_1,m_2+n_2+2)+G_\tau{}^{j_1+2}R_\tau{}^{j_2+k_2+2}H_\tau(m_1,m_2+n_2)\},$$

$$\int f(m_1j_1,1)f(n_1k_1,1)(1/r_{12})f(m_2j_2,2)f(n_2k_2,2)dv_{12}$$
$$=(\pi^2R^5/8)\sum_\tau(2\tau+1)\{R_\tau{}^{j_1+k_1}R_\tau{}^{j_2+k_2}H_\tau(m_1+n_1+2,\gamma_2,m_2+n_2+2,\gamma_2)-R_\tau{}^{j_1+k_1}R_\tau{}^{j_2+k_2+2}$$
$$\times H_\tau(m_1+n_1+2,m_2+n_2)-R_\tau{}^{j_1+k_1+2}R_\tau{}^{j_2+k_2}H_\tau(m_1+n_1,m_2+n_2+2)$$
$$+R_\tau{}^{j_1+k_1+2}R_\tau{}^{j_2+k_2+2}H_\tau(m_1+n_1,m_2+n_2)\}.$$

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The Approximations Involved in Calculations of Atomic Interaction and Activation Energies

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The assumptions underlying the computation of interaction energy among several atoms, and especially of activation energies, have been analyzed and discussed for the case of small overlapping of the one-electron wave functions involved. Some formal justification has been found for several types of approximation which have hitherto been used without adequate examination. Computations of the energy of several three-electron systems are presented as material illustrating the applicability of some of the assumptions to typical cases. It is concluded that in general any modification of the complete Heitler-London treatment of the system may lead to errors comparable in magnitude to the quantity to be computed. The so-called "semi-empirical method," which involves many such modifications, owes its success to a happy cancellation of errors, and, until some theoretical explanation of this cancellation is found, it must assume the status and responsibilities of a purely empirical method.

1. ANALYSIS AND DISCUSSION OF APPROXIMATIONS

THERE have recently appeared numerous papers[1] attempting to predict activation energies of simple chemical reactions, by a method which is essentially a generalization of that first applied by Heitler and London[2] to the problem of two hydrogen atoms, with certain additional approximations. The starting point was an article by London[3] giving an equation for the reaction energy of a system containing three electrons in three orbits having spin degeneracy only. London does not give the derivation of his equation, and, although he states that it is an approximation, he does not discuss the nature or magnitude of the omitted terms. His equation has been extended to more electrons by Eyring and his collaborators, also without examination of the approximations involved. It seems very desirable to subject the whole method to a more careful study.

Analysis reveals that, as usually employed, the method of computing reaction energies between several atoms involves, from the theoretical point of view, the following assumptions:

(A) That a useful result could be obtained by a rigorous application of the H.-L. method, integrating the complete energy operator (as distinguished from the interaction or perturbation terms alone) over a function built up from the unperturbed atomic functions, and then subtracting the unperturbed energy.

(B) That each atom may be represented by one or more "bonding" electrons, having definite individual orbits. Electrons in inner shells, and even "non-bonding" electrons in the same shell, may be neglected.

(C) That the result of a computation based on assumptions (A) and (B) would differ only by small terms from that given by the London formula, or its appropriate extension.

(D) That, in the London formula, those terms which arise from the exchange of two electrons are the same as they would be if these two electrons and their corresponding nuclear charges were the only bodies present, while terms arising from permutations of more than two electrons are negligible.

(E) That the division of the binding energy of a molecule like H_2 into "coulomb" and "exchange" terms has some significance aside from the H.-L. approximate method of computation, so that values of the latter more accurate than those given by calculation can be estimated from spectroscopic binding energies.

Our primary interest lies in the last three assumptions, and we may dismiss the first two with brief mention. Assumption (A), as is well understood, is applicable if the interaction energy of the system is small in comparison with the energy required to raise the unperturbed system to the

[1] For example, Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931); Rollefson and Eyring, J. Am. Chem. Soc. **54**, 170 (1932); Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932); Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933); Eyring, Sherman and Kimball, J. Chem. Phys. **1**, 586 (1933).

[2] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

[3] London, Zeits. f. Elektrochemie **35**, 552 (1929); see also *Sommerfeld Festschrift*, Hirzel, p. 104.

next lowest energy state of the same symmetry. To judge from results, this condition is not well met. The H.-L. method applied to H_2 at the equilibrium distance gives about two-thirds the proper binding energy; with Li_2 the result is worse, previous excellent agreement with experiment[4] having been obtained by neglecting the inner electrons. Nevertheless the method is certainly useful as a qualitative guide, and presumably is more accurate for activation energies, as the internuclear distances are somewhat greater, and the perturbation smaller.

As to assumption (B), the approximate treatments of such problems, in which only spin degeneracy is assumed, agree that so long as triple exchanges are negligible non-bonding electrons should produce a repulsion. If, owing to directed valence, the bonding orbits overlap much more than the non-bonding, the repulsions may be small compared to the attractions; but the methods based on the London formula explicitly neglect directional effects. When assumption (E) is used to estimate "empirical exchange terms" the errors associated with assumption (B) may be partly cancelled. Thus, if one takes 90 percent of the total binding energy to represent the exchange term of the binding electrons for two atoms at a certain distance in the absence of a third atom, this will be numerically smaller than the "real" exchange term, because the repulsion of non-bonding electrons will have been included. On bringing up a third atom and using the London formula, one may expect this modification to result in a partial duplication of the effect of the non-bonding electrons, because they probably continue to repel, though to a different degree. These remarks do not necessarily apply to all the cases which have been treated, since orbital degeneracy is in general present, and in the presence of inner shells the triple exchange terms may be very important. For instance, in a treatment of Li_2 one of us[5] has found that the non-bonding electrons of the inner shells exert an attractive effect in the $^3\Sigma$ state, this arising from the commonly neglected triple exchange terms.

It is to be noted that if the non-bonding electrons are to be eliminated from consideration it is essential to use only the perturbation operator. A discussion of the approximation involved in the neglect of the other terms in the complete energy operator is to be found elsewhere;[5] it is in many cases not unsatisfactory. The approximation of then neglecting non-bonding electrons can be treated by the methods indicated in the discussion of assumptions (C) and (D). The result of applying only the second of these approximations with operators involving atomic terms in the energy along with wave functions including only the bonding electrons, in a treatment like that of assumption (A) is quite different, and cannot be similarly justified. We shall not pursue the subject further, and in what follows shall consider only systems with one electron per atom.

Assumption (C) involves the justification of the London formula. For three electrons, the formula is

$$\epsilon = C - a - (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha)^{\frac{1}{2}}. \quad (1)$$

Here, ϵ is the interaction energy, C is the sum of the Coulomb terms of the three pairs of orbits, α, β, γ, are the corresponding exchange integrals, and a is a term involving a triple exchange. It seems to be generally believed that this formula (omitting the term a) can be obtained by applying the H.-L. treatment in full, and then throwing out all terms which would vanish if the three orbits were mutually orthogonal; that is, by regarding the lack of orthogonality as an accidental matter, of small importance. Thus Slater[6] gives formally the complete solution, and upon discarding terms arising from non-orthogonality, gets an expression which is formally the same as London's. (It is in reality very different, since the terms which it contains involve the whole energy operator, while London's contain only the interaction operator.) That this view of the matter is definitely wrong, will become apparent as soon as one remembers that it is precisely because the orbits are not orthogonal that the H.-L. method succeeds in predicting binding. If all terms due to non-orthogonality are systematically rejected, then the exchange terms will come out positive and repulsion will result. Indeed, the whole basis of the Slater-Pauling theory is the exten-

[4] Bartlett and Furry, Phys. Rev. **38**, 1615 (1931).
[5] James, J. Chem. Phys. **2**, 794 (1934).
[6] Slater, Phys. Rev. **38**, 1109 (1931).

sive overlapping of orbits, and in general orbits which largely overlap will be far from orthogonal. If the London formula (without a) is limited to cases of inappreciable overlapping, it will be useless for computing activation energies. It is possible, as we shall now show, to formulate an argument justifying its use under somewhat less rigorous restrictions. At the same time, we shall find similar justification for assumption (D).

It will be best to start with the two-electron problem. The London formula becomes

$$\epsilon = C + \alpha, \tag{2}$$

while the complete solution is (in Slater's notation)

$$W = [(ab/H/ab) + (ba/H/ab)]/(1+s^2), \tag{3}$$

where s is the integral $\int abdV$, and may be taken as a measure of the degree of overlapping, or of lack of orthogonality. For large separations, s will be small compared to unity; as the centers approach, it will grow, reaching values of the order of one-half in many problems at the equilibrium distance. We shall regard s as a small quantity, developing the discussion in terms of the powers of s to which the various magnitudes are comparable.

To convert (3) formally into (2), we must drop s^2 in comparison with 1, which we are apparently at liberty to do. In fact, however, this will involve an error comparable to the quantity which we wish to calculate. Let us write

$$W = W^\circ + \epsilon, \tag{4}$$

where W° represents the unperturbed energy. Now, ab is a solution of

$$H^\circ(ab) = W^\circ ab, \tag{5}$$

(H° being the unperturbed operator), so that the two terms in the numerator of (3) have for their principal parts W° and s^2W°, respectively, the first being therefore much the larger. By omitting s^2 in the denominator, we make an error of the order s^2W°. But, as we shall see, the whole binding energy is of the second order in s, so that we cannot begin by simplifying the denominator of (3). We must first apply the well-known device of splitting off the unperturbed energy, expressing the operator as the sum of H° and H', the latter containing only the perturbation terms. Owing to (5), we then get

$$W = W^\circ + [(ab/H'/ab) + (ba/H'/ab)]/(1+s^2), \tag{6}$$

where the expressions in the numerator are now exactly the C and α of (2).

The terms in H' are of the same general nature as those in H° (except for the Laplacian in the latter). $C = (ab/H'/ab)$ might therefore be expected to be comparable to $W^\circ = (ab/H^\circ/ab)$. True, it should be somewhat smaller, because the distances involved in H' refer to particles in different atoms, and are therefore larger than those in H°, referring to particles in the same atom; but the ratio should not be as small as s, for s in general goes down as the negative exponential of the interatomic separation, which enters H' only as the minus first power. By a similar argument, we should expect $\alpha = (ba/H'/ab)$ to be comparable with $(ba/H^\circ/ab) = s^2W^\circ$. (In this case the distances involved in H' and H° are the same.) Actually, however, we find that C is much smaller than α, due to extensive cancellation of terms, so that the whole numerator in (6) is of the second order in s; we may therefore pass to the London formula by dropping s^2 in the denominator, with an error of the order $W^\circ s^4$, or ϵs^2, making ϵ numerically too large; this tends to compensate the error fundamental to the H.-L. method. It remains to find out why the cancellation among the terms of C is so much more effective than among those of α, so that we may make predictions for more complex cases which have not been actually computed. To this end we expand C and α (using a notation developed by one of us[7] in a previous paper)

$$C = A/B - aa/B - A/bb + aa/bb;$$

$$\alpha = s^2A/B - s[ab/B + A/ab] + ab/ab.$$

In a purely formal way, these expressions may be rewritten

$$C = (A - aa)/(B - bb);$$

$$\alpha = (sA - ab)/(sB - ab). \tag{7}$$

This draws attention to the fact that each integral may be regarded as the total mutual energy of two electrical distributions, each of zero total

[7] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

charge. In the case of C, each distribution is so arranged that the diffuse negative charge very effectively screens the concentrated positive charge. The mutual energy of two such charges is therefore doubly small; *we have here the reason why the Coulomb term is at least two orders smaller than superficial analysis suggests.* In the case of α, there is no such perfect screening: the exchange integral is small because each of the charges involved is separately small.

[In this analysis it has been tacitly assumed that the wave functions are positive everywhere, or at least in the region of important overlapping. This will be true of bonding orbits. With non-bonding orbits, where nodes occur in the region of overlapping, the factor s may be exceptionally small, or zero, due to cancellation of positive and negative contributions, and will not serve as a basis of reference for orders of magnitude.]

We now examine the case of three electrons in three orbits. Upon separating off the unperturbed energy, we obtain the complete expression for the interaction energy in a form identical with that given by Slater for the total energy:

$$
\begin{aligned}
&\epsilon=(N+2\sqrt{M})/D,\\
&N=P(p-q-r)+Q(q-r-p)+R(r-p-q),\\
&M=P^2qr+Q^2rp+R^2pq+PQ(r-p-q)r\\
&\qquad\qquad +QR(p-q-r)p+RP(q-r-p)q,\\
&D=p^2+q^2+r^2-2pq-2qr-2rp,\\
&P=C-a+\alpha-\beta/2-\gamma/2,\\
&Q=C-a+\beta-\gamma/2-\alpha/2,\\
&R=C-a+\gamma-\alpha/2-\beta/2,\\
&p=1-\pi\kappa\rho+\pi^2-\kappa^2/2-\rho^2/2,\\
&q=1-\pi\kappa\rho+\kappa^2-\rho^2/2-\pi^2/2,\\
&r=1-\pi\kappa\rho+\rho^2-\pi^2/2-\kappa^2/2.
\end{aligned}
\tag{8}
$$

P, Q, R, and p, q, r, respectively, are the diagonal matrix elements of H' and of 1 over the three wave functions which correspond to electron-pair bonds between atoms $B-C$, $C-A$, and $A-B$, respectively. (We have interchanged Slater's assignments of Q and R in order to get a symmetrical permutation scheme.)

$$
\begin{aligned}
&\pi=\int bcdV,\quad \kappa=\int cadV,\quad \rho=\int abdV,\\
&C=(abc/H'/abc)=(A-aa)/(B-bb)\\
&\qquad +(B-bb)/(C-cc)+(C-cc)/(A-aa),\\
&2a=(abc/H'/bca)+(abc/H'/cab)\\
&\quad=\kappa(\rho A-ab)/(\pi B-bc)+\rho(\pi B-bc)/(\kappa C-ca)\\
&\qquad +\pi(\kappa C-ca)/(\rho A-ab)+\rho(\kappa A-ac)/(\pi C-cb)\\
&\qquad +\pi(\rho B-ba)/(\kappa A-ac)+\kappa(\pi C-cb)/(\rho B-ba),\\
&\alpha=(abc/H'/acb)=\alpha_2+\alpha_3,\\
&\beta=(bca/H'/bac)=\beta_2+\beta_3,\\
&\gamma=(cab/H'/cba)=\gamma_2+\gamma_3,\\
&\alpha_2=(\pi B-bc)/(\pi C-bc);\\
&\alpha_3=\pi[(A-aa)/(\pi B+\pi C-2bc)].
\end{aligned}
\tag{9}
$$

Insofar as the non-orthogonality integrals π, κ, ρ, may all be regarded as small quantities of the first order, we see that the Coulomb term C is, as before, a subordinate term of the second order, due to self-screening. In fact, it is identically the sum of the three C's corresponding to the three two-electron problems. The components of the triple-exchange term, a, have the form: small factor times integral very similar to the α term in the two-electron problem (7). The only difference is that the two diffuse charges are not now coincident; they do, however, more or less overlap, since they contain one wave function as a common factor. This term is, then, of the third order. Of the remaining exchange integrals α, β, γ, the parts α_2, β_2, γ_2 are identically the exchange terms of the respective two-electron problems. The terms α_3, β_3, γ_3, have the form: small factor times what may be called a semi-Coulomb integral, since it is the mutual energy of a self-screened distribution and two poorly-screened but small distributions. They are, therefore, presumably of the third order. Since both C and α are commonly negative in the two-electron problem, the analysis just completed leads us to expect that all the integrals in the three-electron problem will likewise be negative.

Since P, Q and R contain no terms larger than the second order, we shall make no error of order higher than the fourth if we follow Slater in introducing the approximation $p=q=r=1$, and this gives just the London formula. (It should be

noticed, however, that Slater was not justified in taking this step before separating off the unperturbed energy; also, that this is not equivalent to assuming the vanishing of the non-orthogonality integrals π, κ, ρ, which must be retained in calculating the separate terms, according to (9).) With three electrons, as with two, the relative accuracy of the London approximation (compared to the strict H.-L. computation) should be of the order of the square of the non-orthogonal integrals. But we can no longer predict the sign of the error, which depends upon the ratios of the various integrals. Thus, if one bond predominates greatly in strength, the problem will naturally approach the simple two-electron problem, and the error will be similar. If two bonds are equivalent, and stronger than the third, as in the problem of three H atoms in a line at equal distances, the formulas become extremely simple. Thus, if atom B is in the center, we have $\pi=\rho>\kappa, |\alpha|=|\gamma|>|\beta|$, and hence

$$\epsilon=[Q-4R]/[q-4r]$$
$$=[C-a+\gamma-\beta]/[1-\kappa\rho^2+\rho^2-\kappa^2]. \quad (10)$$

The London formula omits everything after 1 in the denominator. If ρ greatly exceeds κ this will produce the same kind of error as with two electrons; otherwise the error may be much less. If all three bonds are equivalent, we have

$$\epsilon=R/r=[C-a]/[1-\rho^3]. \quad (11)$$

Here the error caused by omitting ρ^3 is of opposite sign, and of higher order.

This analysis provides formal justification for the London approximation for two and three electrons, and could doubtless be extended to more complex cases. If, however, we wish to go still further and adopt assumption (D) which must be done if we are to put into the London formula integrals which have been calculated for the simple two-electron problems (or taken from diatomic spectra with the aid of assumption (E)) we must further neglect the third-order terms a, α_3, β_3, γ_3. This will lead to more serious errors, especially in the case of the triple-exchange term, which always comes in with the same sign, while the semi-Coulomb terms partly cancel each other.

With regard to assumption (E), little can be said, since it appears to be completely without theoretical justification. The concepts of Coulomb and exchange terms are inseparable from the point of view which regards binding energy as a small perturbation, incapable of distorting the atomic wave functions. This point of view reaches its perfect expression in the strict H.-L. treatment. As soon as the atomic wave functions are modified in any way in constructing the molecular function the whole treatment breaks down, since we can no longer separate off the atomic energy and work with a perturbation operator, but must compute the whole energy of the system and then subtract the atomic energy from the answer. Even if the modified molecular wave function is of a type which assigns the electrons to orbits associated with the individual nuclei, so that the resulting expression for the whole energy contains some terms in which the electrons remain stationary, while in others they make transitions, there is no unique way of determining from these the C and α of the H.-L. method, since we do not know what fraction of the atomic energy to subtract from each part. If the molecular wave function contains ionic terms, or terms in which each electron is shared by both nuclei (as in the principal terms of the best function which we have found for H_2) the whole discussion is meaningless. Similar statements can be made about the problem of three atoms, and it is wholly gratuitous to assume that the relation between the true energies in the two- and three-body problems is of the form given by the H.-L. treatment for approximations to these energies. All that can be said is that the results of the latter are certainly numerically too small in both cases (provided they are negative in sign), so that any process by which they are increased will improve the results, if not carried too far. The use of exchange integrals numerically larger than those computed, whether derived from spectra or by purely arbitrary increase, is such a process.

It appears, then, that the use of approximations A, C and D, together with empirical or calculated exchange integrals, should give good relative accuracy for widely separated atoms, where the non-orthogonality integrals are actually small. But for calculating equilibrium or activation energies this condition is not well

met, and it becomes important to have actual information concerning the errors introduced by the various assumptions. We have therefore made some computations to illustrate the matter.

2. Illustrative Computations

The first computation refers to three H atoms in a straight line, at equal distances 1.7 a_0, the critical configuration in the reaction $H_2+H=H+H_2$, according to Eyring and Polanyi. The strict H.-L. calculation proceeds according to Eq. (10), with the following computed values, with which are compared the corresponding "empirical" values, as selected by those authors from spectral data. Values are expressed in kg cal. per mol:

Integral	C	a	β_2	β_3	α_2, γ_2	α_3, γ_3	κ	π, ρ
Computed	−25.1	−44.8	−14.7	−8.7	−93.1	+0.5	0.275	0.669
Spectral	−21.5	0	−18.1	0	−87.3	0	0	0

In order to illustrate the effects of the separate classes of terms on the result, we present the energy as computed with several selections of terms, first without, and then with, inclusion of the factor $1-\kappa\rho^2+\rho^2-\kappa^2$ (having the value 1.249) which forms the denominator in (10). (See Table I.) These values represent the total mutual energy of the three atoms. The quantity of principal interest is the difference between this and the energy of H_2 in its lowest vibrational state (−66 computed, −103 from spectra). This difference is, for the activation configuration, the activation energy. Since the activation configuration would have to be determined separately for each method of approximation our values cannot be interpreted immediately in terms of predicted activation energies.

Table I. *Values of ϵ, in kg cal. per mol.*

Terms included	$-\epsilon$ without factor	$-\epsilon$ with factor
γ_2, β_2	78.4	62.7
γ_2, β_2, C	103.5	82.9
γ_2, β_2, a	33.6	27.0
γ_2, β_2, C, a	58.7	47.0
γ_2, γ_3, β_2, β_3	69.2	55.4
γ_2, γ_3, β_2, β_3, C	94.3	75.5
γ_2, γ_3, β_2, β_3, a	24.5	19.6
γ_2, γ_3, β_2, β_3, C, a	49.5	39.7
Spectral β_2, γ_2, C	90.1	——

Assumption (A) gives $\epsilon=-39.7$. Adding assumption C changes this to −49.5. Inclusion of assumption (D) further depresses the result to −103.5, and stable H_3 is predicted. The spectral value −90.1 should be compared, not with −103.5, but rather with −82.9, since, in estimating the spectral exchange terms, the authors deliberately neglected the factor $1+s^2$ in hope of compensating partially the error due to neglecting the corresponding factor in the London formula. We have seen that this is reasonable where, as in this case, the two equivalent bonds greatly preponderate over the third. We may compare the result of the strict H.-L. computation, $66-39.7=26.3$ with the "semi-empirical" value $103-90.1=12.9$, and, with due caution, with the experimental value of 7.2 for the activation energy. In this case it is clear that the "semi-empirical" method neglects terms which are separately much larger than the quantity sought; its success is due to extensive cancellation of the errors.

The computation of triple-exchange and semi-Coulomb integrals is exceedingly laborious in the present state of the art, and we have not undertaken the calculation of other examples expressly for the purposes of this article. It is instructive, however, to make use of certain material in the previous computation on H_2O, which, though not corresponding to any actual three-electron problem, will be typical of certain such cases.

We first consider that A and C are hydrogen atoms in the normal state, and B a fictitious atom having all electrons negligible except for a single electron in a 2-quantum s orbit like that of an oxygen atom. The distances $B-A$, $B-C$ are each 2 a_0, and lie at right angles, so that the $A-C$ bond is now not greatly weaker than the others. Eq. (10) applies as before. In the second example, the B atom shall consist essentially of a $2p$ electron of the Slater-Pauling type, the axis directed towards the A atom. The symmetry is now destroyed and we must go back to Eq. (6). Moreover, one of the non-orthogonal integrals is now identically zero, because of the node in the p orbit.

The required quantities are

Integral	C	a	α_2	α_3	β_2	β_3	γ_2	γ_3	π	κ	ρ
s-orbit	−28.3	−31.2	−49.3	−6.2	−30.8	−7.5	−49.3	−6.2	0.456	0.384	0.456
p-orbit	−40.4	+ 5.2	+13.7	0.0	−30.8	−9.7	−15.8	−0.4	0.000	0.384	0.328

and the result of the calculation is

Approximations	B	B and C	B, C and D
s-orbit	−14.6	−14.3	−46.8
p-orbit	−82.0	−92.5	−79.5

The success of approximation C in the case of the s-orbit is due to the fact that the factor which it neglects, $1-\kappa\rho^2+\rho^2-\kappa^2$, is here 0.981, or practically unity, because of the approximate equality of all three bond strengths.

3. Status of the "Semi-Empirical" Method

Our results indicate that in treating 3-electron systems the approximations usually applied in the computation of activation energies involve the neglect of terms of very considerable importance. The results of such computations cannot, therefore, be considered as *bona fide* predictions of quantum mechanics. The further extension of the ideas arising from these simplified computations to the treatment of more complicated systems is also noted to be without theoretical justification. It follows that the relation of quantum mechanics to the so-called "semi-empirical" method is merely suggestive, rather than justificatory.

There can of course be no logical objection to the application of this method as a purely empirical one; as such its justification can arise from its effectiveness in dealing with a large number of special problems. From this point of view it has in fact attained a very remarkable degree of success. It is indeed surprising that in a fairly large number of cases a reasonable degree of accuracy has been obtained through what is, from a theoretical point of view, the cancellation of a number of serious and apparently unrelated approximations. We have noted how several of these tend to counteract each other, but quantitative considerations of this cancellation are as yet entirely lacking.

Perhaps the most important use of the "semi-empirical" process lies in its indication as to which of two alternative chemical processes may be responsible for a chemical change. One may reasonably hope that in the computation of the activation energies of two similar reactions the errors due to the approximations may be similar, so that the sign of the difference of the two activation energies will come out correctly, if that quantity is not too small. The way in which this difference depends on certain of the approximations, such as the variable choice of a ratio for the coulomb and exchange integrals, can be ascertained. In the absence of similar tests of the influence of the other approximations the determination of the limits within which confidence in this process is justified must likewise await the accumulation of empirical evidence.

Two Theorems Concerning Electrolytes

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(Received August 9, 1934)

(1) Fluctuations in the average total electrostatic energy E of the free ions of an electrolytic solution as calculated by the theory of Debye and Hückel are negligibly small in accessible concentration ranges. If $\delta E = \{\bar{E}^2 - (\bar{E})^2\}^{\frac{1}{2}}$, then $\delta E/\bar{E} = (-kT/2\bar{E})^{\frac{1}{2}}$; i.e., the ratio of the fluctuation in energy to the total energy is of the order of the square root of the ratio of the kinetic energy per degree of freedom of a *single molecule* to the *total* electrostatic energy of the system. (2) A general relationship connecting free energy F and average electrostatic energy $\bar{E}$ is derived; for the case where the average potential around an ion is given by the Debye-Hückel formula, $F = 2\bar{E}/3$.

RECENT calculations[2] have been presented which showed that fluctuation terms in the electrostatic potential around a given ion become comparable to the mean value of this potential at low concentrations and hence the validity of the Debye-Hückel[3] limiting law for electrolytes was apparently questioned. In view of the general importance of the Debye-Hückel result as a means of interpreting and correlating experimental data on strong electrolytes, it seems advisable to re-examine the fluctuation terms. Halpern's calculations do show that the fluctuations in potential around a *single* ion can become comparable with the Debye average value for the potential, but this result could perhaps have been foreseen without calculation. Of much greater interest is the fluctuation in the total average electrostatic energy of the system; after all, experiment is concerned with this quantity and not with the behavior of a particular ion. We should expect that a satisfactory method of calculating the average total energy would show negligible fluctuations as long as the total energy was large compared to kT. It can readily be shown that the energy calculated by the method of Debye and Hückel satisfies this requirement at accessible concentrations in solvents of high dielectric constant. In solvents of low dielectric constant, the same conclusion is reached, if the charges in short range ion pairs be excluded in calculating the ionic strength.

1. Distribution of Ions in Solution

Suppose we are given a solution containing N positive ions of charge $+\epsilon$ and N negative ions of charge $-\epsilon$ in a total (large) volume V. In order to obtain information concerning the interionic distances (which are necessary in calculations of potential and energy), we consider the probability of existence of a general ion pair[4] defined as follows: a positive ion i and a negative ion j within a range dr at r constitute an ion pair associated with the distance r, provided there is no unpaired negative ion k at a distance $r_{ik} \leq r_{ij}$ from i. The corresponding probability function $G(r)$ has in general two peaks as a function of r when the concentration is moderately low. The first lies at $r = a$, where a is the average diameter of the ions (which are assumed spherical). This peak is very sharp, because it is due to an exponential function $\exp(\beta/r)$, where

$$\beta = \epsilon^2/DkT, \tag{1}$$

in the region where $r < \beta$. At a distance given approximately by the Bjerrum[5] radius $\beta/2$, $G(r)$ has a minimum. The second peak is a maximum at a distance $\rho \approx \sqrt[3]{V/2\pi N}$, a distance which corresponds in order of magnitude to the distance between uniformly distributed particles. Distances much greater than ρ are very improbable on account of a factor $\exp(-2r^3/3\rho^3)$ which appears in $G(r)$. The maximum at ρ always appears at low concentrations; the peak at $r = a$ appears only if

$$b > 2, \tag{2}$$

where

$$b = \epsilon^2/aDkT. \tag{3}$$

In water, $b = 2$ corresponds to $a = 3.5 \times 10^{-8}$ cm, so for ions (including solvation shells) as large or

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[2] Halpern, J. Chem. Phys. **2**, 85 (1934).
[3] Debye and Hückel, Phys. Zeits. **24**, 185 (1933).
[4] Fuoss, Trans. Far. Soc. **30**, 967 (1934).
[5] Bjerrum, Kgl. Danske Vidensk. Selskab. **7**, No. 9 (1926).

larger than this value, ions in contact always represent the *least* probable configurations.[6] The large fraction of the solute will have interionic distances of the order of ρ. But ions at this distance automatically satisfy, at small concentrations, the condition

$$\epsilon^2 e^{-\kappa r}/rDkT \ll 1 \tag{4}$$

necessary for the validity of the Debye-Hückel treatment. When $b>2$, (4) is still valid for ions whose distances reckoned pairwise are near the peak at ρ, but it does not hold for ions whose distances are of the order of a. Ions in these configurations, however, are short range pairs, whose external field approximates that of a *dipole* at distances larger than a. We therefore exclude in first approximation this group of ions in calculating the long range interionic effects. (In second approximation, we take them into account by means of the triple ion[7] interaction.) Short range pairs are defined as those for which $a \leq r \leq d$, where d is a distance equal to the thickness of a layer of several solvent molecules; its precise value is left to be determined by experiment. As long as $d \geq 2a$, the definition is sufficient to account for a large fraction of the ions for which $a \leq r \leq \beta/2$, and which do not satisfy the condition (4). We shall consider ions for which $r>d$ as free ions, and calculate their effect on the properties of the solution by means of the Debye-Hückel time average method, and rely on the fluctuation theorem to be proved below for the accuracy of the result.

2. Fluctuations in Energy

We define the excess free energy F due to the potential energy of the free ions by the equation

$$e^{-F/kT} V^m = \int e^{-E/kT} d\omega, \tag{5}$$

where $d\omega$ includes integration over the elements of volume $dx\,dy\,dz$ for each of the m free ions ($m=2N$ for complete absence of short range pairs, i.e., "complete dissociation") and E is the total potential energy of the free ions. Fowler,[8] Kramers[9] and Onsager[10] have emphasized the importance of including the "van der Waals energy" in E, in order that the integral (5) converge. We therefore set

$$E = E_c + E_w, \tag{6}$$

where E_w is the non-Coulomb energy and

$$E_c = \tfrac{1}{2} \sum_j{}' \sum_k \epsilon_j \epsilon_k / D r_{jk}. \tag{7}$$

In (7), r_{jk} is the distance between two ions of charge ϵ_j and ϵ_k and the prime on the first summation sign indicates that all $j=k$ terms are omitted. (We may obviously omit the intrinsic energy $\epsilon^2/2aD$ of each ion because we are not concerned with F as a function of temperature.) The bilinear form (7) may be replaced in the conventional way by the linear form

$$E_c = \tfrac{1}{2} \sum_i \epsilon_i \psi_i, \tag{8}$$

where

$$\psi_i = \partial E_c / \partial \epsilon_i = \sum_j{}' \epsilon_j / D r_{ij} \tag{9}$$

is the instantaneous potential at a particular ion of charge ϵ_i, due to all of the other free ions present.

Differentiation of (5) with respect to ϵ_i gives $\bar{\psi}_i$, the mean value of ψ_i

$$\bar{\psi}_i = \partial F / \partial \epsilon_i = V^{-m} \int e^{(F-E)/kT} \psi_i d\omega. \tag{10}$$

Multiplying (10) by $\epsilon_i/2$ and summing over all ions gives

$$\bar{E}_c = \tfrac{1}{2} \sum_i \epsilon_i \bar{\psi}_i \tag{11}$$

for the average value of the Coulomb energy.

[6] The argument is of course subject to the approximations implied in the model used to represent the electrolytic solution. Described very briefly, it comprises uniformly charged spheres of diameter a in a homogeneous medium of dielectric constant D and viscosity η. The important physical approximations involved are the charge distribution in the ionic sphere (cf. Kirkwood, J. Chem. Phys. **2**, 351 (1934)) and the use of the macroscopic dielectric constant D for small distances. The error in the latter approximation is absorbed in a, which is chosen large enough to include rigidly oriented solvent dipoles, for which the effective dielectric constant is unity in order of magnitude. Fowler's phrase "omnium gatherum" seems to the writer to be the most descriptive term yet applied to the parameter a.

[7] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 2387 (1933).

[8] Fowler, Trans. Far. Soc. **23**, 434 (1927).

[9] Kramers, Amsterdam Proc. **30**, 145 (1927).

[10] Onsager, Chem. Rev. **13**, 73 (1933). This reference contains an investigation of the fluctuation terms which explicitly includes the effects of van der Waals forces.

Differentiation of (11) with respect to ϵ_k and rearrangement of the result gives

$$\tfrac{1}{2}\sum_i \epsilon_i \partial\bar{\psi}_i/\partial\epsilon_k = \bar{\psi}_k/2 + [\bar{\psi}_k \cdot \bar{E}_c - \overline{(E_c\psi_k)}]/kT, \quad (12)$$

(where $i=k$ must be included in the summation the left). We now multiply (12) by ϵ_k and sum over all ions, obtaining after rearrangement

$$(\delta E)^2 = \overline{(E_c - \bar{E}_c)^2} = \frac{kT}{2}\left(\bar{E}_c - \tfrac{1}{2}\sum_k \epsilon_k \sum_i \epsilon_i \frac{\partial\bar{\psi}_i}{\partial\epsilon_k}\right). \quad (13)$$

This equation gives an explicit expression for the fluctuation in total electrostatic energy. It is derived (without qualifying assumptions or approximation) from the definition of F in (5), the classical expression for E_c in (7) and the definition of ψ_i in (9) simply by means of mathematical manipulation.

Now let us test the result of Debye and Hückel by means of Eq. (13). We shall assume that the concentration is so small that we may use the limiting form of their equation

$$\bar{\psi}_i = -\epsilon_i\kappa/D + O(\kappa^2) \quad (14)$$

for the *mean value* of the potential around an ion of species i, even if at these concentrations the instanteneous value of the potential around a particular ion of species i does exhibit fluctuations comparable with $\bar{\psi}_i$ itself.[2] That is, we assume that (14) gives the correct mean value of potential which is to be used in calculating the total average electrostatic energy by means of the summation (11). We shall find that the value of E_c calculated in this way shows only negligible fluctuations, unless the solution is so dilute that the total energy E_c is of the order of kT.

The parameter κ in (14) depends on the total number of ions present. We shall change the conventional formulation somewhat, in order to emphasize the fact that it depends on the charge of each ion present, by writing

$$\kappa^2 = 4\pi\sum_i \epsilon_i^2/VkDT, \quad (15)$$

where the summation now extends over all free ions counted individually, instead of over all ions counted by species. For example, for a symmetrical electrolyte $\Sigma\epsilon_i^2 = m\epsilon^2$; if the number of short range pairs is negligible, $\Sigma\epsilon_i^2 = 2N\epsilon^2$.

By differentiation of (14), we find

$$\frac{\partial\bar{\psi}_i}{\partial\epsilon_k} = -\frac{\kappa}{D}\delta_{ik} - \frac{\epsilon_i}{D}\frac{\partial\kappa}{\partial\epsilon_k}, \quad (16)$$

where $\delta_{ik}=1$ when $i=k$ and vanishes for $i\neq k$. Differentiation of (15) gives

$$\partial\kappa/\partial\epsilon_k = 4\pi\epsilon_k/\kappa DkTV. \quad (17)$$

Substituting (17) in (16) and the result in (13) gives

$$(\delta E)^2 = -kT\bar{E}_c/2,$$

or

$$\delta E/\bar{E}_c = (-kT/2\bar{E}_c)^{\frac{1}{2}}, \quad (18)$$

where

$$\bar{E}_c = -\kappa\sum_i \epsilon_i^2/2D = -kTV\kappa^3/8\pi. \quad (19)$$

Combining (18) and (19) gives

$$\delta E/\bar{E}_c = (4\pi/V\kappa^3)^{\frac{1}{2}}. \quad (20)$$

Now as concentration approaches zero, $V\kappa^3$ approaches zero so that in the limit of zero concentration, (20) becomes infinite, i.e., the fluctuation terms become dominant even in the energy.

Two facts must, however, be borne in mind. First, the effects of Coulomb forces appear experimentally as deviations from ideal behavior, and second we can only measure properties of all of the ions present. Eq. (18) already shows that the fluctuations are not serious as long as

$$\bar{E}_c \gg kT/2 \quad (21)$$

as was pointed out in the introduction.

We now investigate numerical values, in order to see when this inequality is reversed. We have

$$\kappa = 2.92\times10^8(c\gamma/D)^{\frac{1}{2}}, \quad (22)$$

where $c\gamma$ is the concentration of free ions in equivalents per liter. (Here γ is the fraction of salt existing as free ions, $0<\gamma\leq1$). In (20), $\bar{E}_c$ is the average energy of m free ions and V is the volume containing them. If we take $m=2L=2\times6.06\times10^{23}$, then $V=1000/2c\gamma$. Substituting these values, we find

$$-kT/2\bar{E}_c = 1.01\times10^{-27}D^{\frac{3}{2}}(c\gamma)^{-\frac{1}{2}}.$$

In practical cases, D will not exceed 100 in order of magnitude, giving

$$\delta E/\bar{E}_c \leq 10^{-12}/(c\gamma)^{\frac{1}{2}}. \quad (23)$$

The fluctuations will amount to 10 percent at a concentration of free ions $c\gamma = 10^{-44}$, and $\delta E/\bar{E}_c$ will be unity when $c\gamma = 10^{-48}$. These concentrations appear to be inaccessibly small.

The conclusion we reach, therefore, is that the Debye-Hückel time average method will give accurate results when applied to the calculation of the properties of electrolytic solutions, insofar as they are due to the presence of free ions. The method will fail only at concentrations so low that the thermodynamic properties of the solution are so near those of the solvent that it is pointless to speak of deviations from ideal behavior. For example, the osmotic coefficient $(1-\epsilon^2\kappa/6Dkt)$ for a 1–1 salt equals $(1-0.4\sqrt{c})$ in water. At 10^{-4} N, this is 0.996, so that an error of only 0.1 percent in observed freezing point depression is already a 25 percent error in the interionic correction term. (The author hopes that this will not be interpreted as an "indeterminism principle"; the point of the argument is that fluctuations in unobservable quantities have no physical significance while, at accessible concentrations, the fluctuations in the observable quantities are negligible.)

3. Relation Between Average Energy and Free Energy

In calculating free energies of electrolytic solutions, it is customary to use a charging process at some step in the procedure. Herewith is presented a proof of the theorem

$$F = 2\bar{E}/3, \quad (24)$$

which seems to be more straightforward than some of the earlier proofs.

We consider an electrolytic solution, in which all charges are linear functions of a parameter σ, where $0 \leq \sigma \leq 1$. Then by (7)

$$E(\sigma) = \sigma^2 E_0, \quad (25)$$

where $E(\sigma)$ is the total electrostatic potential energy of any instantaneous configuration of ions and E_0 is the value corresponding to $\sigma = 1$. If the potential energy arises by the charges being built up from 0 to σ, then

$$E(\sigma) = \int_0^\sigma \frac{dE(\sigma)}{d\sigma} d\sigma = \int_0^\sigma 2E(x)\frac{dx}{x}. \quad (26)$$

Furthermore

$$\bar{E}(\sigma) = V^{-m} \int \exp\{[F(\sigma) - E(\sigma)]/kT\} E(\sigma) d\omega, \quad (27)$$

where $F(\sigma)$ is defined by the equation

$$\exp(-F(\sigma)/kT) V^m = \int \exp(-E(\sigma)/kT) d\omega. \quad (28)$$

Differentiation of (28), and use of (26) gives

$$dF(\sigma)/d\sigma = (2/\sigma)\bar{E}(\sigma). \quad (29)$$

Differentiation of (27), and use of (26) gives

$$\frac{d\bar{E}(\sigma)}{d\sigma} = -\frac{2}{\sigma}\bar{E}(\sigma) + \frac{\bar{E}(\sigma).\ \bar{E}(\sigma) - \overline{E(\sigma)^2}}{\sigma kT/2}. \quad (30)$$

If we now substitute (18) in (30), we obtain

$$d\bar{E}(\sigma)/d\sigma = (3/\sigma)\bar{E}(\sigma),$$

whence

$$F(\sigma) = 2\bar{E}(\sigma)/3. \quad (31)$$

When $\sigma = 1$, (31) gives the standard result (24). The result depends on explicit use of the Debye-Hückel potential.

The author takes this opportunity to thank Professor R. H. Fowler for valuable suggestions in regard to the treatment of these theorems.

On the Structure of Monolayers of Myristic Acid. Erratum.

(J. Chem. Phys. 2, 574, 1934)

In Fig. 1 of this paper, there is an error in the ordinate scale. The correct figure is published here.

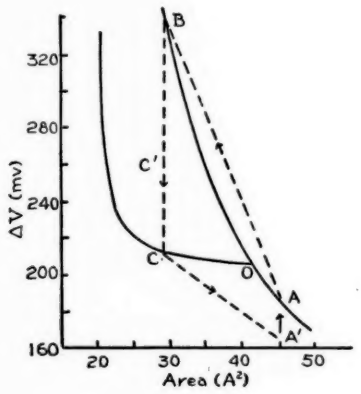

FIG. 1.

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LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Complex Formation Due to Polarization

Glockler, Roe and Fuller,[1] in a recent paper under the above title, have investigated the behavior of gaseous mixtures of Kr and HCl, to determine whether the polarization of the former by the polar molecules of the latter is sufficient to yield evidence for the formation of complex molecules. They obtain for B in the familiar equation $PV=RT+BP$, the expression $B=-0.00168N_1^2-0.00097N_1N_2-0.00445N_2^2$ at $T=328.7°$K. N_1 and N_2 are the mole fractions of Kr and HCl, respectively. They conclude from the fact that the coefficient of N_1N_2 is not zero that there is interaction between the unlike molecules which is equivalent to complex formation. We wish to point out, however, that any pair of molecules, like or unlike, should show a van der Waals attraction, and to express the opinion that only an attraction in excess of this should be interpreted as the effect in question. Such an excess does not appear to be present between the unlike molecules in the mixture investigated.

We have calculated the force coefficients for pure Kr and pure HCl by the aid of equations derived by Lennard-Jones,[2] assuming the attraction exponent to be 7 and the repulsion exponent to be 11. The use of any other probable exponent would not alter our conclusion. If the usual assumption is made that $\lambda_{12}=(\lambda_{11}\lambda_{22})^{\frac{1}{2}}$ where the λ_{12} represents the force constant for unlike molecules, and λ_{11} and λ_{22} those for like molecules, we get for the coefficient of N_1N_2 the value -0.0164, much larger than the experimental value of -0.00194. The evidence is therefore against the existence of action between Kr and HCl beyond the normal van der Waals attraction.

The reason for the excess of the calculated over the measured coefficient of N_1N_2 is doubtless to be sought in the fact that λ_{22} is enhanced by the polarity of the HCl

molecules leading to $\lambda_{12} < (\lambda_{11}\lambda_{22})^{\frac{1}{2}}$, as well as in the partial inapplicability of the equations of Lennard-Jones. The mixture in question doubtless belongs to the type frequently encountered in the liquid state (where the molecular crowding brings out clearly the effects of molecular fields) which deviates positively from the ideal solution laws, often to the extent of forming two liquid phases.

We admit that the difference between our point of view and that of Glockler and co-workers is largely one of definition. The division of intermolecular forces into distinct types is doubtless rather arbitrary but we believe that if one is to admit one type, such as polarization forces, one can hardly avoid considering the van der Waals forces which arise from electron interaction regardless of the presence of dipole forces.

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September 21, 1934.

[1] George Glockler, C. P. Roe and D. L. Fuller, J. Chem. Phys. **1**, 703 (1933).
[2] Lennard-Jones, Proc. Roy. Soc. London **A106**, 463 (1924); **115**, 334 (1927).

Complex Formation Due to Polarization Definition of a Molecule

In the foregoing note Hildebrand and Wood express that the system Kr-HCl contains no complex structures but that the interaction between the unlike molecules is due to van der Waals forces only. I am indebted to Professor Hildebrand for his kindness in letting me see their remarks before publication.

I would like to reply as follows: To the view that the interaction between a krypton atom and an HCl molecule is no more due to complex formation than is the interaction between two krypton atoms I would readily subscribe. The difference of our points of view is one of definition only as Hildebrand and Wood state. I would like to take this opportunity to express my view regarding the matter of molecule formation and the definition of a molecule.

The complete picture of the interaction by two hydrogen atoms as described by Eisenschütz and London[1] shows that the two atoms at large distances react towards one another by attractive forces (interpreted as the van der Waals forces) and as they approach they disturb one another more and more, exchange-forces between the electrons come into play and the forces of valency will finally hold the two atoms together into a molecule. Even though the approach be in the antisymmetric state, still, at large distances, the two atoms will have a potential minimum (very small, only 0.001 e.v. at about 2A). Two helium atoms approaching one another will also show a potential minimum. They will not form a molecule of great stability to be sure; but there is possible a situation (potential minimum) where no forces are acting between the two helium atoms (neither repulsion or attraction, $dV/dr=0$).

Now the question arises: What structure shall we call a molecule? I am tempted to define a molecule as "*any configuration of two or more atoms, simple molecules or radicals which show a potential minimum.*" This will include all coordination compounds and simple molecules of the nonpolar and polar type. I do not think that this definition is too broad. It leads me to suppose that there exist molecules of varying stability. I am thinking of a whole series of structures to be called molecules. On one end of the series I would place the structure (He-He) made up of two helium atoms held together by van der Waals forces only and on the other end of the series I would place such a perfect molecule (in the ordinary sense) as H_2. However in between these two extremes I can think of a whole gradation of interactions and I believe no sharp break exists in the series mentioned. One cannot tell, in a given case somewhere in the middle of the series, whether valency forces or van der Waals forces are the predominant character of the force holding the structure together.

For when one considers the analysis of Eisenchütz and London concerning the approach of two hydrogen atoms then one sees that the reason the energy comes out as a sum of terms

$$E=E_1+E_2+\cdots$$

is because we have made it so. It is because we had to solve the problem by perturbation methods that the result has been produced in the form of a series. And then we interpret the first approximation as valency-forces (Heitler-London) and the second term as polarization interaction[2] and so forth. How would the story read had we been able to solve the mathematical problem of the wave equation for two atoms completely without recourse to perturbation theory and without approximation? I believe the solution would be such that the various forces (at large and small distances) would merge into one another in a way that we could *not distinguish them and separate them into classes* depending on distance such as valency forces and van der Waals forces.

Many ideas come to my mind but I would like to mention two more points of argument. In the case of adsorption for example one finds oxygen adsorbed on tungsten with an enormous heat of adsorption (valency forces according to Langmuir) and for example argon adsorbed on KCl (held by London forces as per F. V. Lenel[3]). Some heavy organic molecules decompose on heating and do not evaporate, because the interaction between molecules is greater than the bonding between the parts or greater than the activation energy needed to cause them to decompose. In this connection I am reminded of a paper by Briegleb[4] where similar views are put forth.

When one then considers the above view one gets the idea that any interaction between two atoms is a sign of incipient molecule formation. So two krypton atoms interact to be sure very feebly but nevertheless krypton is an imperfect gas and the second virial coefficient $B_{11}\neq 0$. *And so if B_{12} for HCl-Kr mixtures is greater than zero then the two unlike atoms show a beginning tendency to interact.*

The main idea I wish to present is the view that the separation of the forces acting between atoms into valency

forces, van der Waals forces and others is artificial. Since there is no sharp break in the series of possible forces acting between various atoms and molecular systems I feel constrained to include even weakly bound complexes into the family of structures called molecules. I realize that the broad meaning given the term causes it to lose significance but I see no quantitative criterion whereby one could define precisely the meaning of the term "molecule."

I hope to discuss these ideas in more detail at a future date.

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Minneapolis, Minnesota,
September 21, 1934.

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The Transformation of Formic Acid by Irradiation of Its Aqueous Solution with X-Rays

Our earlier work[1-4] on the chemical properties of the activated water molecules, which are produced by the irradiation of water with x-rays, has been extended by a study of the chemical changes resulting from the irradiation of dilute solutions of formic acid. The transformation of the formic acid was studied by gas analysis for carbon dioxide and hydrogen. For concentrations of formic acid below one milli-molar/1000 cc, the amounts of these gases produced are independent of the formic acid concentration. A dependence on the hydrogen ion concentration exists, as shown in Fig. 1, where the micro-mols of hydrogen and carbon dioxide formed per 1000r of dosage and per 1000 cc of solution are given as functions of the pH. Below pH = 3.0, equal volumes of hydrogen and carbon dioxide are obtained corresponding to the simple decomposition: $HCOOH = CO_2 + H_2$. For increasing values of the pH, the carbon dioxide production decreases to zero while the hydrogen is reduced to approximately one-half its former value which indicates that the principal reaction at large

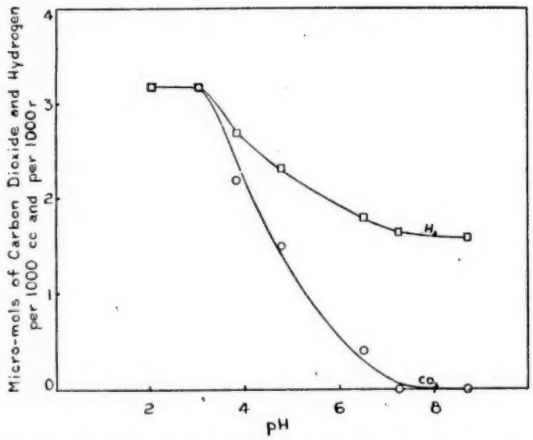

FIG. 1. The production of carbon dioxide and hydrogen as functions of the pH of the irradiated solution.

pH is: $2HCOOH = (COOH)_2 + H_2$. This change of chemical effect occurring as the hydrogen ion concentration is changed is associated with the change of the formic acid molecule from the neutral to its ionized form.

For concentrations of formic acid from 1 to 200 milli-molar/1000 cc, the amount of carbon dioxide increases while the hydrogen remains constant. It appears that this increased production of carbon dioxide is due to the setting in of a chain reaction, but no evidence as to its exact nature has been procured.

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